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DEVELOPMENT OF TREATMENT AND CONTROL TECHNOLOGY FOR REFRACTORY PETROCHEMICAL WASTES

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows, (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries, and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American people.

William C. Galegar

William C. Galegar, Director
Robert S. Kerr Environmental
Research Laboratory

ABSTRACT

This summary document presents the results of research and development work pertaining to the treatment of biorefractory organic pollutants emanating from petrochemical processing plants. Specifically, it covers application of the unit operations of (1) carbon adsorption, (2) steam stripping, (3) solvent extraction, and (4) ozonation to a number of process effluents from halogenated hydrocarbon, isocyanate, acetylene, and styrene manufacturing industries.

In the carbon adsorption study, different commercial activated carbons were evaluated via Freundlich isotherms for streams containing C_1 and C_2 chlorinated hydrocarbons in quantities less than 1000 mg/liter. Subsequent field trials were conducted to yield breakthrough data.

Steam stripping evaluations were made for process effluents containing chlorinated hydrocarbons and aromatic hydrocarbons. This unit operation removed up to 75 percent of the TOC present in the raw process effluent. Data for a commercial design were obtained from a pilot demonstration unit. Commercial design specifications were prepared for installation of a unit at one of the participating companies.

Solvent extraction evaluations were made for process effluents containing chlorinated hydrocarbons and aromatic hydrocarbons. The best solvent for maximum removal of organics with minimum TOC residuals in the extracted effluent was a straight-chain paraffin hydrocarbon in the C_{10} to C_{12} range.

Ozonation evaluations were initiated to determine if chemical oxidation with ozone was feasible as a pretreatment method for biorefractory industrial wastewater. Complete oxidation with ozone would be uneconomical, but the partial oxidation of refractory wastes to a biodegradable form with ozone could be economically competitive. Ozonation was proved to be an effective method of pretreating wastewaters from the manufacture of toluene diisocyanate, ethylene glycol, styrene monomer, and ethylene dichloride. Batch biooxidation studies showed ozonation improved the biotreatability of these industrial wastes.

In addition to these unit operation evaluations, a study was undertaken to develop an activated carbon from a by-product soot which results from the manufacture of acetylene. Quantities of raw soot were dried, pretreated, pelletized, and activated to yield a product with commercial potential which had about 80 percent as much adsorption capacity as a similar commercial product.

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SECTION I

INTRODUCTION

In 1969, the Water Quality Administration authorized a study to evaluate all point sources of effluents discharging to the Mississippi River from St. Francisville to Venice, Louisiana. The study period included the last two quarters of 1969 and all of fiscal 1970 and 1971. This study focused attention on the need to develop best practicable treatment for the more difficult-to-treat effluents from several of the major chemical plants in the area.

The initial concept of this study was to utilize the combined efforts of the Louisiana State Science Foundation, participating industrial companies, Gulf South Research Institute (GSRI), and university assistance to develop technology for biological and physical-chemical treatment of industrial effluents to achieve desired goals of reducing contaminant loadings. The major objectives of the project were...

...*to develop and demonstrate* effluent treatment procedures for the reduction of refractory petrochemical effluents with presently available water treatment technology.

...*to develop* an economical source of activated carbon from a waste carbon by-product stream.

...*to analyze* present and projected loadings, treatment levels, and treatment costs.

Both laboratory bench and in-plant pilot scale equipment were used. The major processes investigated were: carbon adsorption with regeneration evaluation; solvent extraction; biological treatment (aerobic and anaerobic); ozone oxidation; steam stripping; and compounding and activation of a soot carbon by-product. Parallel with these efforts was work to develop an economical and commercial source of activated carbon from a waste soot carbon by-product. Research was also directed toward development of a better and more economical method to regenerate spent activated carbon. These regeneration studies were made on the developed carbon and on commercial carbons. To meet the objectives of this program, nine project work areas were identified and described:

1. Process evaluations and point source identification.
2. Waste characterization.
3. Bench-scale process feasibility studies.
4. Carbon preparation, activation, and regeneration procedures.
5. Pilot plant studies.
6. Analytical services.
7. Analysis of loadings, treatment levels, and treatment costs.
8. Supporting services and studies.
9. Evaluation of results and recommendations.

SECTION 2

CONCLUSIONS

Several different unit operations were evaluated on a total of 21 individual plant process effluents for their effectiveness in removing contaminants present in the wastewater. Steam stripping evaluations were made on process effluents containing chlorinated hydrocarbons and aromatic hydrocarbons. This unit operation removed up to 99 percent of the chlorinated hydrocarbons and up to 75 percent of the total organic carbon (TOC). Residual TOC was in the form of chloral, which includes aldehyde and hydroxy-type chlorinated organics resulting from the oxychlor process. This type of treatment process would cost $0.0005 per liter of wastewater or about $0.05 per kilogram of product.

Solvent extraction evaluations were made on process effluents containing chlorinated hydrocarbons and aromatic amines. Carbon disulfide, tetrachloroethane, pentane, cyclohexane, and freon had little effect on removing chlorinated hydrocarbons. Removal of aromatic amines by tetrachloroethane, pentane, cyclohexane, octane, dodecane, dichlorobutane and tetrachlorobutane never exceeded 50 percent. A C_{10}-C_{12} straight-chain paraffin was found to be effective in removing the chlorinated organics. This solvent also exhibited low residual solubility (15 mg/liter) in the extracted water. This type of treatment process would cost $0.0005 per liter of water treated and $0.066 per kilogram of ethylene dichloride produced.

Activated carbon adsorption evaluations were made on process effluents containing chlorinated hydrocarbons, aromatic amines, and aromatic hydrocarbons. Four commercial activated carbons (Calgon, Barneby-Cheney, Witco, and Westvaco) were found to be effective in removing chlorinated organics and aromatics from wastewater. Spent carbon was regenerated with steam. In the resulting readsorption tests, the regenerated carbon exhibited over 90 percent of fresh carbon activity.

A soot carbon by-product was evaluated as a potential activated carbon. From this study, a carbon was developed which had about 80 percent of the activity of commercial samples. Sufficient material was produced to conduct isotherm and breakthrough tests on several different contaminated effluents.

Ozonation was shown to be an effective method of pretreating biorefractory wastewaters. The biorefractory compounds in toluene diisocyanate, ethylene glycol, and ethylene dichloride contaminanted process wastewaters were oxidized to a biodegradable form. Ozonation was found to improve the biotreatability of water containing styrene by transforming it to a compound such as benzoic acid. The ozonation of styrene reaction products, benzaldehyde, and benzoic acid were affected by both solution pH and temperature.

SECTION 3

RECOMMENDATIONS

Each of the unit operations tested under this grant program showed a capability for removing wastewater contaminants to a greater or lesser degree. The work under this grant should be expanded to cover the following aspects of reducing contaminants in industrial process effluents.

The ozonation of industrial effluents showed that refractive organics can be converted to a biodegradable state. Further development work should be carried out to establish dosages and optimize process conditions.

Ozonation changed the basic characteristics of the organic components and could have an effect on carbon adsorption activities. Further work should be considered for utilizing ozonation as a pretreatment process.

The project concentrated on evaluating each separate unit operation and its effect on reducing the contamination in the process effluents. Very little consideration was given to evaluating the effect of using two of these processes in series. The possibility of utilizing such a series of unit operations to treat some of the process effluents should be investigated. As a result, the operation and capital cost for each treatment step could be optimized.

Although an activated carbon was developed from the Monochem soot carbon, neither the resulting material nor the manufacturing procedure was optimized. Additional studies should be undertaken to follow up this development.

Additional joint federal, state, and industrial projects would be of value to achieve optimized, cost-effective treatment systems for all the various industrial process effluents.

SECTION 4

PROGRAM SUMMARY

PROCESS EVALUATIONS AND POINT SOURCE IDENTIFICATION

Among the 20 point source samples studied, several originated from the same process operation. In addition, several of the companies in the program manufactured the final product under similar processing conditions. The manufacturing processes investigated are listed in Table 1.

TABLE 1. MANUFACTURING PROCESSES

Product		Process
Ethylene dichloride	via	direct chlorination
Ethylene dichloride	via	oxychlorination
Perchloroethylene and 1,1,1-trichloroethylene	via	chlorination of ethylene dichloride
Ethyl benzene	via	alkylation of benzene
Toluene diamine	via	polymerization of dinitrotoluene
Polyols	via	polymerization of ethylene oxide
Acetylene	via	combustion of methane
Methylcellulose	via	propylene oxide

Ethylene dichloride (1,2-dichloroethane) via chlorination

Ethylene dichloride (1,2-dichloroethane) is the largest volume organic chlorine derivative. Domestic production in 1974 was over 5 billion kg. The greatest single outlet for ethylene dichloride (EDC) is for the production of vinyl chloride. There are 16 major producers of ethylene dichloride; of these, 8 are located on the Louisiana Gulf Coast. These 8 companies produce slightly more than 55 percent of the total production (Table 2).

Production of EDC from ethylene and chlorine (Fig. 1) can be represented by the following equation:

$$C_2H_4 + Cl_2 \longrightarrow ClCH_2CH_2Cl \qquad (1)$$

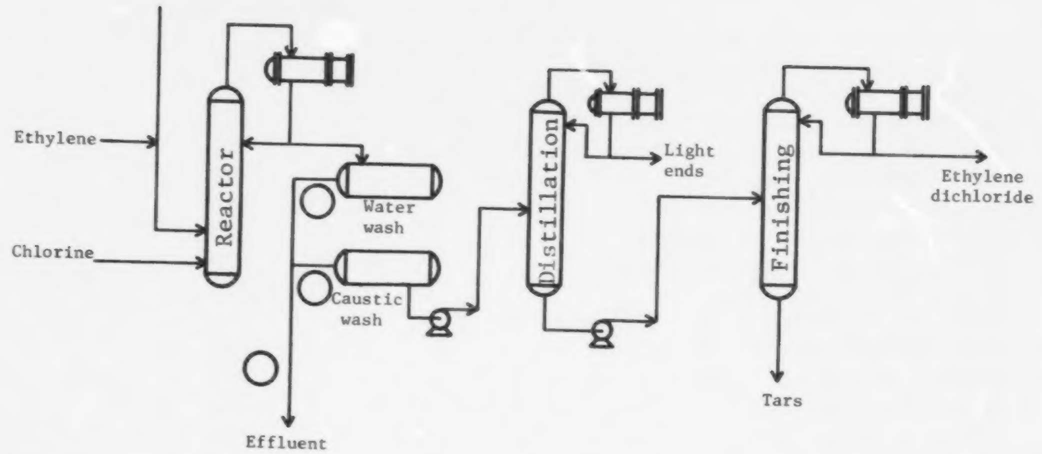

Ethylene
Chlorine
Reactor
Water wash
Caustic wash
Effluent
Distillation
Light ends
Finishing
Ethylene dichloride
Tars

Figure 1. Manufacture of ethylene dichloride via direct chlorination of ethylene.

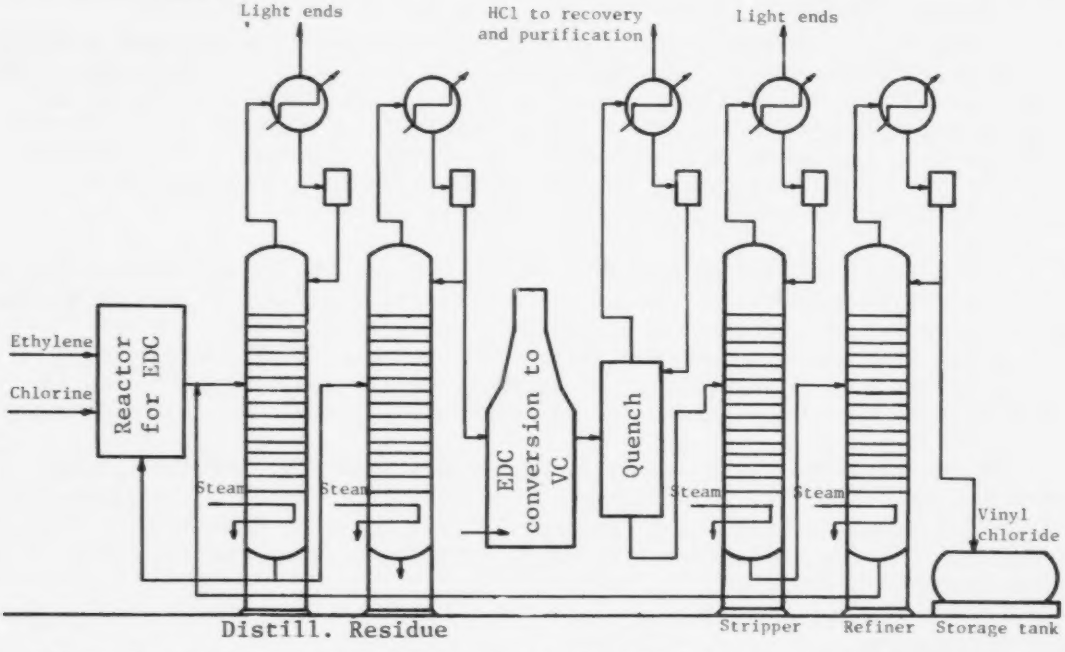

Light ends
HCl to recovery and purification
Light ends
Ethylene
Chlorine
Reactor for EDC
Steam
Steam
EDC conversion to VC
Quench
Steam
Steam
Vinyl chloride
Distill. Residue
Stripper
Refiner
Storage tank

Figure 2. Ethylene dichloride and vinyl chloride monomer manufactured with HCl recovery.

TABLE 2. ETHYLENE DICHLORIDE PRODUCTION

Producer	Capacity (million kg/yr)
Allied, Baton Rouge, Louisiana	270
American Chemical, Long Beach, California	105
Conoco, Lake Charles, Louisiana	545
Diamond Shamrock, Deer Park, Texas	45
Dow, Freeport, Texas	590
Dow, Oyster Creek, Texas	500
Dow, Plaquemine, Louisiana	525
Ethyl, Baton Rouge, Louisiana	225
Ethyl, Houston, Texas	110
Goodrich, Calvert City, Kentucky	110
PPG, Guayanilla, Puerto Rico	405
Shell, Deer Park, Texas	315
Union Carbide, Taft, Louisiana	635
Union Carbide, Texas City, Texas	65
Vulcan, Geismar, Louisiana	65
Total	4,630

*Chemical marketing Reporter, vol. 202, No. 21, Nov. 20, 1972.

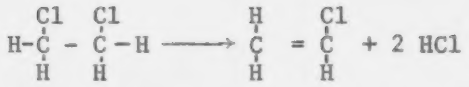
At fairly low temperatures (below 25°C), this addition reaction proceeds to almost 100% conversion. As the temperature is raised, 1,1,2-trichloroethane formation becomes significant. Chlorine can be added in either liquid or vapor phase with or without the aid of a catalyst. Catalysts suggested for this reaction include antimony chloride and ferric chloride. The reaction is generally carried out in an ethylene dichloride solvent which has a catalytic effect in conjunction with the metal salts.

Since this reaction is exothermic, recycle cooling is necessary. One method of cooling is withdrawal of the product in the vapor form, condensing and refluxing. The by-product side effects are controlled by several processing techniques. The chlorine-to-ethylene ratio, the temperature, and the pressure are regulated. In general, the reactor is maintained in the liquid phase, and ethylene and chlorine are injected via sparge nozzles.

By carrying out the reaction at higher pressures (5.25 kg/cm^2), the reaction rate increases perceptably. Side reactions, notably the production of 1,1,2-trichloroethane, also increase. Since there is a market for this by-product as a solvent, faster reaction rates with separation and sale of this product are favored.

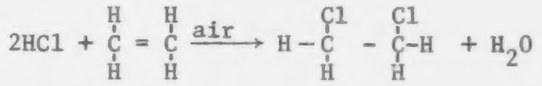
Oxychlorination

With the advent of the market development of vinyl chloride came the problem of disposing of the hydrogen chloride by-product from the dehydrochlorination of ethylene dichloride (see Figure 2).



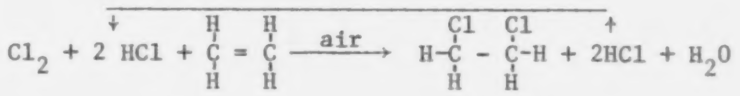
$$\mathrm{H{-}\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}{-}H \longrightarrow \overset{H}{\underset{H}{C}}=\overset{Cl}{\underset{H}{C}} + 2\ HCl} \qquad (2)$$

A process was developed to recycle the hydrogen chloride to make more ethylene dichloride. The technique became known as the oxychlor process.



$$\mathrm{2HCl + \overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} \xrightarrow{air} H{-}\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}{-}H + H_2O} \qquad (3)$$

The next logical step in the development of this technology was the incorporation of reactions (1) and (3).

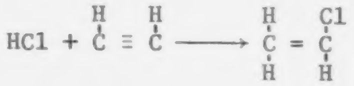


$$\mathrm{Cl_2 + 2\ HCl + \overset{H}{\underset{H}{C}}=\overset{H}{\underset{H}{C}} \xrightarrow{air} H{-}\overset{Cl}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}{-}H + 2HCl + H_2O} \qquad (4)$$

The system to accomplish this process sequence does not vary significantly from the initial chlorine and ethylene reactor system. In a typical reactor, mole ratios of 1:3.3:1.6 oxygen:hydrogen:chloride and ethylene are contacted in a reactor containing aluminum impregnated with copper chloride. Temperatures are in the 300°C range at atmospheric pressure. The reaction products contain approximately 16 mole percent EDC, 72 mole percent water, and 9 mole percent hydrogen chloride. Overall yield of EDC is about 92 percent on ethylene and 98 mole percent on hydrogen chloride. A typical process flow is shown in Figure 3.

Vinyl Chloride from Acetylene

A traditional route to the manufacture of vinyl chloride is the reaction of hydrogen chloride with acetylene.



$$\mathrm{HCl + \overset{H}{C}\equiv\overset{H}{C} \longrightarrow \overset{H}{\underset{H}{C}}=\overset{Cl}{\underset{H}{C}}} \qquad (5)$$

The main by-products of this reaction are 2-chloropropene and some residual tar from the purification operation. The catalyst is a copper based material. The spent catalyst is changed infrequently, with the residual going to landfill. The chloropropene can be recycled to an oxychlor process with chlorine and ethylene as the principal feed materials. This process is rapidly losing its commercial importance bacause of the reduction in acetylene capacity. Major producers of vinyl chloride are listed in Table 3.

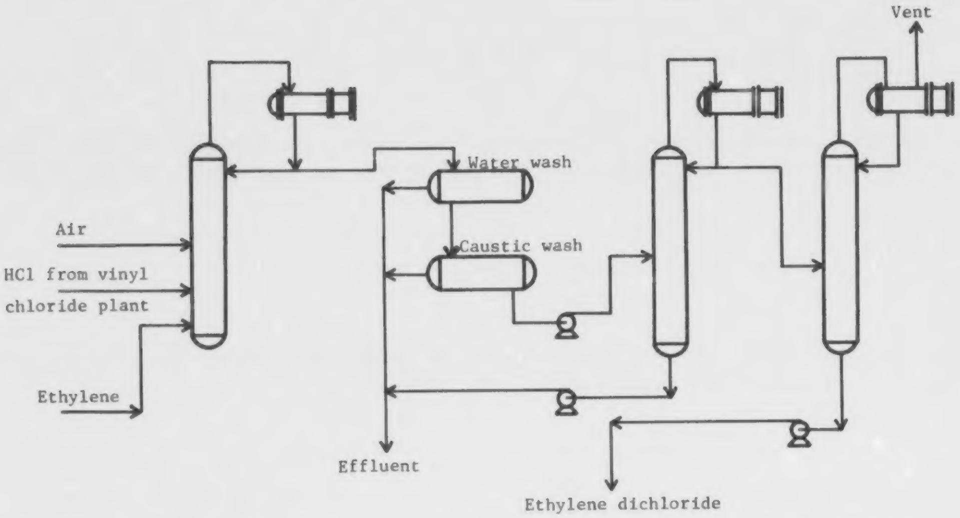

Vent
Water wash
Air
Caustic wash
HCl from vinyl
chloride plant
Ethylene
Effluent
Ethylene dichloride

Figure 3. Manufacture of ethylene dichloride via oxychlorination of ethylene utilizing hydrogen chloride.

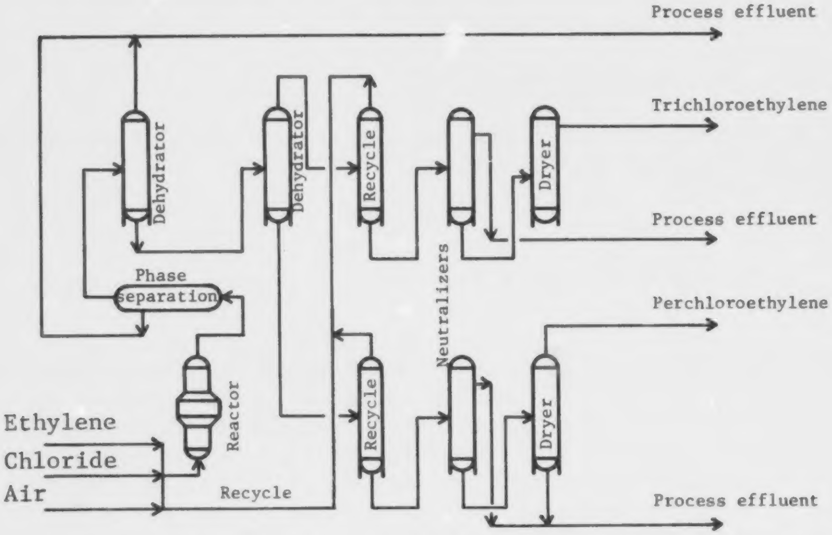

Process effluent
Trichloroethylene
Dehydrator
Dehydrator
Recycle
Dryer
Process effluent
Phase
separation
Neutralizers
Perchloroethylene
Reactor
Recycle
Dryer
Ethylene
Chloride
Air
Recycle
Process effluent

Figure 4. Manufacture of perchloroethylene and trichloroethylene.

TABLE 3. PRODUCTION OF VINYL CHLORIDE*

Producer	Capacity (million kg/yr)
Air Products, Calvert City, Kentucky	65
Air Products, Pensacola, Florida	20
American Chemical, Long Beach, California	65
Borden, Illiopolis, Illinois	60
Borden, Leominster, Massachusetts	80
Conoco, Oklahoma City, Oklahoma	110
Diamond Shamrock, Deer Park, Texas	120
Diamond Shamrock, Delaware City, Delaware	45
Ethyl, Baton Rouge, Louisiana	80
Firestone, Perryville, Maryland	105
Firestone, Pottstown, Pennsylvania	120
General Tire, Ashtabula, Ohio	55
General Tire, Point Pleasant, West Virginia	20
Goodrich, Avon Lake, Ohio	60
Goodrich, Henry, Illinois	60
Goodrich, Long Beach, California	60
Goodrich, Louisville, Kentucky	155
Goodrich, Pedricktown, New Jersey	75
Goodyear, Niagara Falls, New York	45
Goodyear, Plaquemine, Louisiana	45
Great American Chemical, Fitchburg, Massachusetts	20
Hooker, Burlington, New Jersey	80
Hooker, Hicksville, New York	7
Keysor-Century, Saugus, California	16
Monsanto, Springfield, Massachusetts	30
National Starch, Meredosia, Illinois	5
Olin, Assonet, Massachusetts	65
Pantasote, Passaic, New Jersey	25
Pantasote, Point Pleasant, West Virginia	40
Robintech, Plainesville, Ohio	110
Stauffer, Delaware City, Delaware	80
Tenneco, Burlington, New Jersey	75
Tenneco, Flemington, New Jersey	30
Union Carbide, South Charleston, West Virginia	70
Union Carbide, Texas City, Texas	110
Uniroyal, Plainesville, Ohio	60
Total	2,268

*Chemical Marketing Reporter, Vol. 208, No. 2, July 14, 1975.

Manufacture of Perchloroethylene and 1,1,2-Trichloroethylene

An inexpensive fluid bed catalyst with a copper base is used in the reaction below to produce perchloroethylene from ethylene dichloride.

$$C_2H_4Cl_2 + 2Cl_2 \rightarrow C_2Cl_4H_2 + 2HCl$$

To produce trichloroethylene, a portion of the chlorinated organic by-product can be recycled, along with the light ends.

$$C_2H_4Cl_2 + 2Cl_2 \rightarrow C_2HCl_3 + 3HCl$$

Combination production of perchloroethylene and trichloroethylene is shown in Figure 4. In the simultaneous chlorination and dechlorination of ethylene dichloride, dry chlorine and liquid EDC are fed to a fluidized catalyst reactor. Light chlorinated organics are recycled back to the reactor. The crude perchloroethylene is neutralized with a circulating caustic wash stream to remove dissolved HCl. The caustic solution is purged periodically to remove dissolved solids.

TABLE 4. TRICHLOROETHYLENE PRODUCTION*

Producer	Capacity (million kg/yr)
Diamond Shamrock, Deer Park, Texas	27
Dow, Freeport, Texas	68
Ethyl, Baton Rouge, Louisiana	18
Hooker, Tacoma, Washington	14
Hooker, Taft, Louisiana	27
PPG, Lake Charles, Louisiana	90
Total	244

*Chemical Marketing Reporter, Vol. 202, No. 21, November 20, 1972.

After decantation, the crude is dried and the perchloroethylene purified in a two-step distillation system. Light ends are recycled back to the system and the perchloroethylene is taken overhead from the second column. The HCl can be used as a secondary feed to the reactor step with the addition of air or oxygen. The reactor conditions are carefully controlled to selectively produce perchloroethylene.

With different reactor conditions and additional distillation equipment, trichloroethylene can be selectively produced along with the perchloroethylene product. Steam can be generated by circulating condensate through tubes in the reactor. The reactor off-gas is easily condensed with water cooling. Refrigeration loads for secondary recovery are necessary to minimize air pollution. Reaction temperatures are 300° to 400°C with pressures slightly above atmospheric. A typical catalyst would be an active carbon impregnated with cupric chloride.

Ethylbenzene Manufacture

Ethylbenzene is the major raw material for the production of styrene monomer (Fig. 5). A small portion (about 2%) is made by super-fractionation of an aromatics fraction rich in ethylbenzene. The major process for ethylbenzene manufacture involves the reaction of ethylene with benzene in a Friedel-Crafts alkylation reaction.

$$CH_2{=}CH_2{+}C_6H_6AlCl_3 \rightarrow CH_3CH_2C_6H_5{+}AlCl_3$$

A typical reaction system consists of a ceramic lined reactor operating at atmospheric conditions. The fresh benzene is introduced in the bottom of the reactor and the ethylene is sparged into the system. The reactor is usually operated at the boiling point of benzene. Since the reaction is exothermic, the benzene vapors boil overhead and are condensed and refluxed to the reactor. In this manner, the reaction temperature can be controlled.

The reaction system forms a complex with the aluminum chloride. The product, along with the complex, overflows the reactor and goes to a decanting vessel. The complex is a heavy, oily material and readily settles out of the overflow. After settling, the complex is recycled to the reactor. The product is water washed to remove the aluminum chloride and is then "sweetened" with a caustic wash. Purification is by distillation.

There are two effluents of concern in the manufacture of ethylbenzene by alkylation: (1) The overflow from the water washing of the alkylate reactor, which contains soluble aromatics (benzene, ethylbenzene, diethylbenzene, etc.) and aluminum chloride. This overflow is acidic with residual hydrochloric acid (if the pH is adjusted to a basic condition, the aluminum will appear as the hydroxide floc). (2) The benzene feed to the reactor, which is usually predried by azeotropic distillation. The water from this drying operation is decanted.

Styrene

Ethylbenzene is normally made in conjunction with the manufacture of styrene. After purification, the ethylbenzene is preheated in the presence of steam and passed over an iron oxide based catalyst where it is partially converted to styrene. The reaction products are cooled and the oil layer goes to a distillation section. The water is oil stripped and recycled to the steam process. In the distillation section, the styrene is purified by vacuum distillation. A possible effluent source in this area is the vacuum drain from the steam jets. A process innovation would be to recycle these to the dehydrogenation intermediate tank.

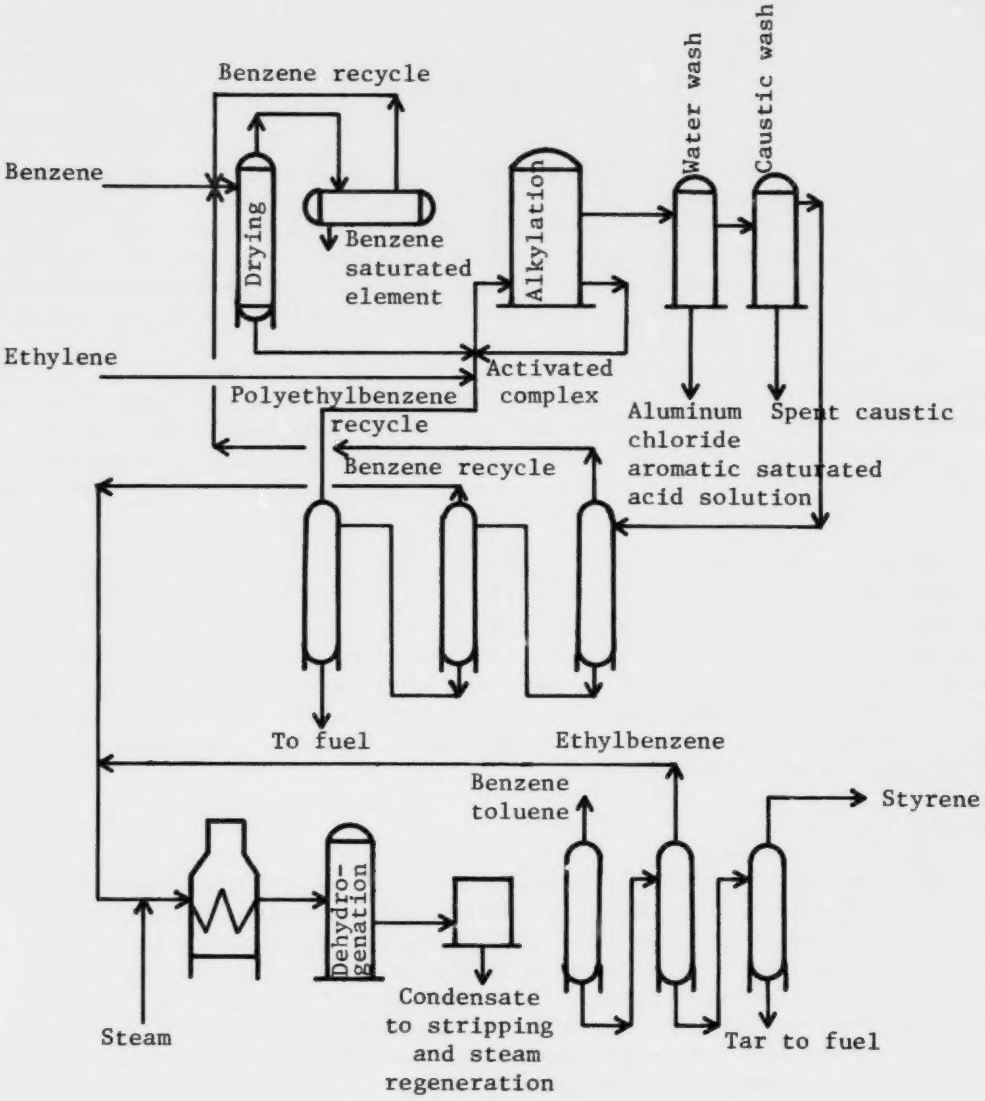

Benzene recycle
Benzene
Drying
Benzene saturated element
Alkylation
Water wash
Caustic wash
Ethylene
Activated complex
Polyethylbenzene recycle
Aluminum chloride aromatic saturated acid solution
Spent caustic
Benzene recycle
To fuel
Ethylbenzene
Benzene toluene
Styrene
Dehydrogenation
Steam
Condensate to stripping and steam regeneration
Tar to fuel

Figure 5. Ethylbenzene and styrene manufacture.

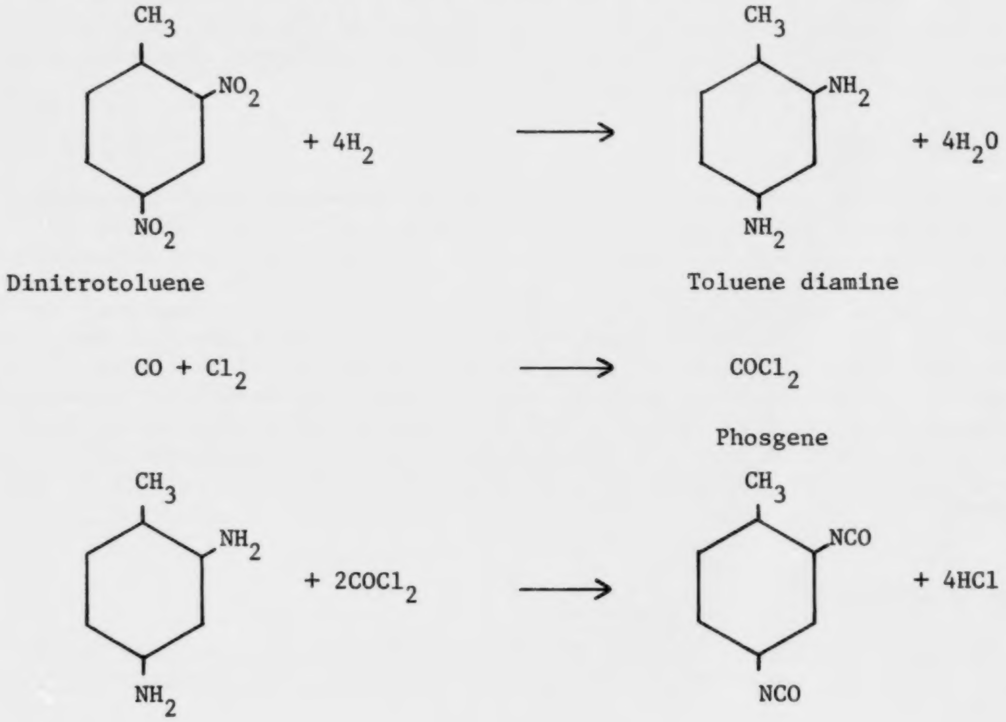
TABLE 5. STYRENE MONOMER PRODUCTION*

Producer	Production (million kg/yr)
Amoco, Texas City, Texas	360
Cos-Mar, Carville, Louisiana	225
Dow, Freeport, Texas	295
Dow, Midland, Michigan	160
El Paso, Odessa, Texas	55
Foster Grant, Baton Rouge, Louisiana	325
Gulf, Donaldsonville, Louisiana	225
Monsanto, Texas City, Texas	360
Shell, Torrance, California	110
Sinclair-Koppers, Houston, Texas	50
Sinclair-Koppers, Kobuta, Pennsylvania	195
Sun (DX), Corpus Christi, Texas	35
Union Carbide, Seadrift, Texas	135
Total	2,530

*Chemical Marketing Reporter, Vol. 201, No. 8, February 21, 1972.

Isocyanate

The manufacture of toluene diisocyanate (TDI) has the following sequential processing steps, starting with dinitrotoluene as the base material.

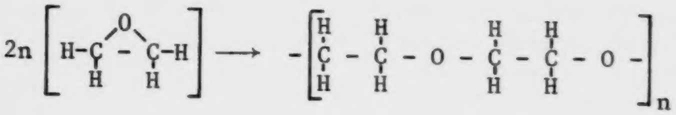

CH3
NO2
NO2
+ 4H2
CH3
NH2
NH2
+ 4H2O
Dinitrotoluene
Toluene diamine
CO + Cl2
COCl2
Phosgene
CH3
NH2
NH2
+ 2COCl2
CH3
NCO
NCO
+ 4HCl

Phosgene is usually generated as needed and is fed to the reactors via a selective solvent where it is reacted with toluene diamine at progressively higher temperatures. The reaction products are first stripped of residual phosgene and hydrogen chloride and then the TDI product is purified via vacuum distillation. The effluent is usually highly colored, but can be treated biologically.

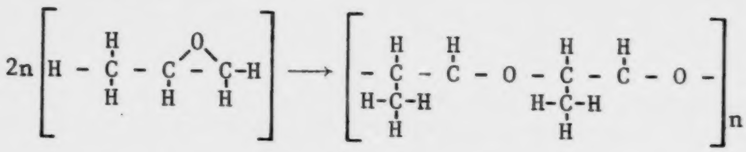
Polyols

Polyols are used primarily in the production of polyurethanes, although they have specific applications themselves. Polyols may be made from two sources:

1. Ethylene oxide



2. Propylene oxide



The reaction generally takes place under pressure in the presence of a solvent. Process effluent consists of an aqueous wastewater saturated with solvent, intermediate and the final product.

Methyl Cellulose

The effluent from a synthetic oxide methyl cellulose process consists of the wash water from the final product cleaning operation. Because the finished product is a solid, cellulosic material, the wash water contains traces of the methyl cellulose. The water will also contain trace amounts of the unreacted raw materials and certain intermediate or incomplete reaction products. The final reaction products in aqueous solution are neutralized, creating a salt solution which contains all of the trace components. Treatment of an aqueous brine solution saturated with relatively nonvolatile components is limited. Steam stripping and solvent extraction can be eliminated from possible consideration, since the suspended solids are nonvolatile, and the cellulose trace components are not very soluble in any solvents.

SOURCE OF EFFLUENTS

The point sources of the individual process effluents included in the program are listed in Table 6. The general nature of each process source is indicated.

TABLE 6. CODED PROCESS WASTEWATER STREAMS

Stream Number	Code Designation	Process Origin
1	011A001	Halogenated hydrocarbons
2	011B001	Halogenated hydrocarbons
3	011C001	Halogenated hydrocarbons
4	041A001C	Halogenated hydrocarbons
5	041BC01	Halogenated hydrocarbons
6	041C001	Halogenated hydrocarbons
7	041D001	Aromatics and organic oxides
8	041E001	Halogenated hydrocarbons
9	041F001	Halogenated hydrocarbons
10	041G001B	Methyl cellulose and hydroxyethers
11	081A001	Halogenated hydrocarbons
12	081B001	Halogenated hydrocarbons
13	081C001	Halogenated hydrocarbons
14	131A001B	Aromatics (quench)
15	161A001C	Halogenated hydrocarbons
16	161B001	Halogenated hydrocarbons
17	161C001	Halogenated hydrocarbons
18	221A001C	Halogenated hydrocarbons
19	221B001	Halogenated hydrocarbons
20	221C001	Halogenated hydrocarbons
21	231A001B	Aromatic amines
22	231B001B	Polyols and oxides
23	351A001B	Aromatics

INDIVIDUAL PROCESS EFFLUENT CHARACTERIZATION

Each of the process effluents was completely characterized before decisions were made as to the type of treatment steps which would be applied to these streams. Individual samples were collected for each stream which were representative of the process conditions and specific tests conducted. Details of the tests performed on each individual process stream are given in Tables 7, 8 and 9.

Since the project extended over a four-year period, a recharacterization of the process streams under investigation was made to check for any effluent variations. A comparison was made of the stream characterizations at the beginning and end of the period.

Analytical Developments

To investigate the effluent with respect to the effectiveness of certain unit operations for contaminant removal, it was necessary to identify specific organic components of the process effluents. Known analytical techniques were not sufficiently commercialized to utilize set procedures. Consequently, it was necessary to develop certain test procedures to quantify these specific organic compounds.

TABLE 7. SOLUBLE ORGANIC STREAM CHARACTERIZATION

Soluble Organics	011A (mg/1)	011B (mg/1)	011C (mg/1)	041A (mg/1)	041B (mg/1)	041C (mg/1)	041D (mg/1)	041E (mg/1)	041F (mg/1)	081A (mg/1)	081B (mg/1)	081C (mg/1)
Methyl chloride	Trace	1.0	736.0	0-40	2.4	2.0			200.0		3.0	2.0
Ethyl chloride	19.7	Trace	0.9	0-30	Trace				Trace			
Vinylidene chloride	1.0		0.8			0.3		2.0	5.7	0.1	1.0	0.1
Trans 1,2-dichloroethylene						0.1						
Cis 1,2-dichloroethylene		Trace	6.0			0.1				10.0		0.5
Chloroform	2.5	0.1	25.0			0.2		0.2	15.6			1.0
Ethylene dichloride	6974.0	2858.0	5755	9122.0	6.0	6.0	6.0	2.0	3.3	6.0	42.0	2.0
Carbon tetrachloride						5.0				1.0	2.0	8.0
Trichloroethylene						3.0				202.0	3.0	84.0
1,1,2-Trichloroethane		17.0										
Perchloroethane										7.0	7.0	20.0
Tetrachloroethane										306.0		
Toluene							2.0					
Benzene							11.6					

TABLE 8. SOLUBLE ORGANIC STREAM CHARACTERIZATION

Soluble Organics	161A (mg/1)	161B (mg/1)	161C (mg/1)	221A (mg/1)	221B (mg/1)	221C (mg/1)	351A (mg/1)
Methyl chloride	3.0	2.0	13.0	2.0	0.2		
Ethyl chloride		6.5	2.7		3.8	21.4	
Vinylidene chloride	10.0	6.5	56.8				
Trans 1,2-dichloroethylene	0.1	19.7	327.4		1.3		
Cis 1,2-dichloroethylene	7.0	64.0	546.3		1.1		
Chloroform	23.0			683.0	0.96		
Ethylene dichloride	200.0	410.0	1077.6	8331.0	9238	54.8	
Carbon tetrachloride						0.21	
Trichloroethylene	6.0	25.5	109.6				
1,1,2-Trichloroethane	40.0	29.6			53.6		
Perchloroethane	14.0	10.4					
Tetrachloroethane							
Toluene							1.2
Benzene							5.65

TABLE 9. STREAM CHARACTERIZATIONS

Stream	COD (mg/l)	TC (mg/l)	pH	Flow (l/min)	Alkalinity as $CaCO_3$ (mg/l)	Acidity as $CaCO_3$ (mg/l)	Chlorides as Cl (mg/l)
011A	3678	1565	12.2	76-227	16000	0	18113
011B	1112	712	1.5	57-151	0	29254	1988
011C	615	1703	11.2	189-416	4840	0	6564
041A	1764	1638	11.7	341-454	1050	0	2662
041B	30	250	2.9	341-454	0	135	408
041C	454	13	2.5	241-454	0	241	762
041D	325	69	6.9	1514-1892	30	10	7
041E	10752	2576	5.8	341-454	376	8	6
041F	18	54	10.5	341-454	325	0	418
041G	23198	7409	10.6	114-227	--	--	28617
081A	6	50	10.6	76-114	1180	0	1
081B	100	17	1.4	76-114	0	2580	1909
081C	390	57	12.1	76-114	12635	0	9685
131A	1050	273	9.5	114	220	0	119
161A	1040	1843	7.7	76-189	304	10	5140
161B	418	148	0.9	57-114	0	0	10557
161C	6279	4390	<0.1	38-95	0	0	77112
221A	16100	9022	0.1	57-114	0	102,312	116,127
221B	11280	10250	<0.1	38-57	0	269,892	107,289
221C	6080	5840	12.7	19-38	31800	0	46
231A	10680	1810	9.7	38-57	1475	0	14
231B	2562	821	11.9	57-95	1140	0	32
061A	463.6	479	11.9	76-151	2060	0	147

During the study period, there were two methods used for analyzing chlorinated hydrocarbons: (1) the vapor-liquid partition technique developed by Dow Research* and (2) a direct liquid injection utilizing a reference component as base identification.

After careful investigation, the partition coefficient method was selected since it offered more flexibility in analyzing different effluents with varying amounts of trace organics.

EFFLUENT TREATMENT

The process effluent characterization data indicated that 17 of the individual wastewater streams were derived from a chlorinated organic process. Even though the individual process effluents came from different plants, the amounts of the chlorinated hydrocarbons in each were similar.

Initially, air stripping trials were intended to indicate which process effluents would create potential emission problems because of the volatile nature of the organics present in the wastewater. The need for this information was obvious where biological treatment was being considered.

Air Stripping Studies

Wastewaters which contain primarily volatile organic compounds pose a problem to biological waste treatment systems which utilize open vessel aeration as a means of dissolved oxygen control. As the wastewater enters the aeration vessel, a major portion of the organic loading is air stripped. An estimate of the volatile and nonvolatile fractions of the organic contamination must be known to interpret data collected during biological treatment studies.

Since the majority of the streams selected for the project are wastewaters from chlorinated solvent processes which contain volatile organics, a study was conducted to determine the effect of aeration alone on the streams' pollutant concentrations.

Results of the air stripping study are shown in Tables 10 and 11. The results indicate that 11 of the 18 streams tested are air strippable in excess of 50 percent of their total oxygen demands. Stream 011C displayed the highest air stripping potential (88 percent), and stream 041C the least (10 percent), based on the TOD analyses of the feed and residual streams. These results show that an efficiently operated steam or air stripping operation can reduce the organic concentration of most of the streams appreciably and in some cases leave relatively biodegradable residual pollutants.

Table 10 shows the results from air stripping of the various industrial waste streams. Total oxygen demand (TOD) of the initial sample and TOD of the residual stream were determined. In column six, the ratio of the BOD_5 to the TOD in the residual is shown. This number is interpreted as the biodegrad-

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*Analytical Method No. QA-466, Dow Chemical, U.S.A., Louisiana Division, Plaquemine, Louisiana 70764.

TABLE 10. AIR STRIPPING AND BOD_5 RESULTS*

Stream	TOD Initial (mg/l)	TOD Residual (mg/l)	TOD Removal (%)	BOD_5 Residual (mg/l)	BOD_5/TOD Residual (mg/l)	Total Carbon Initial (mg/l)	Total Carbon Residual (mg/l)
041A	4260	642	85	247	0.38	--	240
041B	1389	1380	0	37	0.03	300	450
041C	71	64	10	726	--	40	22
041D	510	235	54	61	0.26	225	125
041E	10500	5000	52	2137	0.43	2500	3200
041F	275	140	49	131	0.94	88	53
011A	--	--	--	38	--	1920	215
011B	2200	1950	11	159	0.08	830	825
011C	1230	130	89	44	0.34	830	100
081A	120	92	23	124	--	9	34
081B	260	36	86	11	0.31	124	18
081C	--	--	--	159	--	105	90
161B	500	235	53	61	0.26	67	62
161C	7600	5050	34	1800	0.36	3900	3450
221A	5800	2350	59	1750	0.74	3000	1450
221B	5700	2300	60	1450	0.63	2150	1400
221C	4500	2850	37	2450	0.86	2750	1800
131A	1700	1950	-15	658	0.34	600	600

*Aeration time for all samples was 500 min; each sample was approximately 1 liter. Air flow was not measured. The surface of the reactor was visibly agitated by the air stream entering at the bottom of the reactor. The air flow was designed to simulate a bio-aeration system.

TABLE 11. PERCENT REMOVAL OF VOLATILE ORGANICS BY AIR STRIPPING

Soluble Organics	041A	041B	041C	041D	041E	041F	011A	011B	011C	131A	081A	081B	081C	221A	221B	221C	161B	161C
Low molecular weight volatiles	99.9	100.0	89.9	99.7		100.0	99.9	50.0	100.0	39.6	32.8	98.5		98.6	99.9	100.0		100.0
Vinylidene Chloride	99.9	100.0					91.6											47.5
Cis 1,2-Dichloroethylene	99.8	92.2	93.8				100.0				100.0	99.9						27.8
Trans 1,2-Dichloroethylene																		
Chloroform	99.7	74.2									100.0		97.1					
Ethylene Dichloride	89.5		89.5			99.9	98.3	98.8	95.4	99.4	97.5	99.9	98.8	68.2	99.0	100.0	99.0	87.7
1,1,1-Trichloroethane																		
Carbon Tetrachloride						99.6							99.7					
Trichloroethylene		100.0	99.6			97.8					99.8	99.9	99.9					80.9
1,1,2-Trichloroethane			85.0						89.6	86.9				100.0	99.0			71.1
Perchloroethylene									99.7		100.0	99.9	100.0					32.6
1,1,2,2-Tetrachloroethane									98.2									
Benzene				99.9														
Toluene				99.9														
Xylene				100.0														
Styrene				100.0														

ability of the stream. A ratio close to one would indicate that the residual contaminants after air stripping were easily biodegradable. A very small number would indicate the reverse. The range of this ratio for the various industrial streams varies from 1.05 to a minimum of 0.05.

Carbon Adsorption

To determine if the process effluent stream contaminant loading could be reduced by carbon adsorption with subsequent regeneration, wastewaters from the representative processes were collected and adsorption isotherms experimentally obtained. The results indicated that for streams 041A, 161A, and 221A the chlorinated hydrocarbons were readily adsorbed. The possibility of regeneration with steam in situ was good for these streams. Isotherm and breakthrough data for streams 011A, B, and C, and streams 081A, B, and C were not determined for the preliminary evaluation since these streams exhibit unit operation characteristics similar to the ones for which data were obtained. A preliminary examination of the constituents in streams 041F, 231A, and 231B indicated that these would not be amenable to carbon adsorption. Stream 041F contained some suspended solids and would require prefiltration.

Batch Biological Treatment Evaluations

Evaluation of the biological degradability of the various process effluents was conducted to aid in determining the potential process sequence. These results are shown in column 5 of Table 10. All of the process effluents exhibited biodegradability. Chloral was the main contaminant being biodegraded in the chlorinated hydrocarbon contaminated effluents. The process effluents considered for biotreatment were:

1. Stream 041G - methyl cellulose
2. Stream 131A - quench wastewater blowdown
3. Stream 231A - aromatic amines
4. Stream 231B - polyols
5. Stream 351A - aromatics

Organic Oxide Methyl Cellulose Waste Stream (041G)--

This stream was found to contain high chloride levels averaging 32,339 mg/l, and would require neutralization and supplemental nutrients preceding biological treatment. The high chloride levels inhibited the biotreatability of this process effluent, although it was possible to acclimate a microorganism which would function in this environment. Under typical operating conditions, approximately 60 percent of the BOD_5 could be removed from the inlet water.

Aromatic Wastewater (351A)--

This wastewater contains a high concentration of total dissolved solids (TDS) (70,198 mg/l). The wastewater requires neutralization and supplemental nutrients (nitrogen and phosphorus) prior to biological treatment. Although this process effluent did not exhibit any toxicity toward the microorganisms, the refractive nature of the organics did not permit a total reduction of residual BOD_5 below 60 percent of the incoming stream. Similar results were obtained with streams 231A and 231B.

Solvent Extraction

Since air stripping of the halogenated hydrocarbon contaminated waste water indicated a major portion of the organics would be removed, it is expected most of the organics would be removed by volatilization instead of biological degradation. Air dispersion would not contribute to total environmental removal. As a result of this preliminary evaluation, it was concluded that a unit operation such as solvent extraction might be a suitable pretreatment step or effective enough to remove the organics to desired levels. Several solvents showed promise for this in-process method of reducing the organic contaminants in the process effluent. Feasibility of solvent extraction for four streams is outlined in Table 12.

TABLE 12. FEASIBILITY OF SOLVENT EXTRACTION

Stream Number	Type of Contaminant	Discussion
221A	Halogenated hydrocarbon	Easy to solvent extract. Solvent selection dependent on residual in wastewater and its resulting need for further treatment.
351A	Aromatics	High dissolved solids. Aromatics could be solvent selective.
231A	Aromatic amines	Not amenable to extraction.
231B	Polyols	Some detergent action which could inhibit solvent selectivity.

Preliminary work at Texas A & M University on process effluent samples indicated that a kerosene fraction made from petroleum might selectively extract the chlorinated hydrocarbons present in process effluent. The results suggested that a straight chain saturated hydrocarbon fraction in the C_{12} range might also be selective. This latter solvent might be preferable because of its low solubility in water, as well as its high boiling point, which could be easier to control in a solvent recovery and recycle.

Steam Stripping

The high volatility of the chlorinated hydrocarbons dissolved in the process effluents from this industry group make steam stripping of the wastewater attractive. Because of the low volatility of the residual chlorals, these related compounds will be left in the stripper bottoms. The two factors which affect removal of organic contaminants by steam stripping are: (1) amount of organics present and (2) formation and composition of azeotropic mixtures.

The existence of an azeotrope is not necessarily deleterious to the application of steam stripping for removal of trace organics. If the organic-water mixture going overhead forms two immiscible layers, it is still possible to utilize this approach to controlling contamination of process effluents. The two phases which condense from the overhead can be directed back into the system at different points. The water layer can be refluxed to the top of the stripping column while the organic layer is directed back to an intermediate stage of the process.

An examination of the effect of recycling the organic layer back to process is necessary. If there are undesirable by-products present, the injection of this organic layer must be such that these by-products can be recovered in bottoms or overheads in the subsequent finishing section.

The process effluents under evaluation in this program exhibit the characteristics listed in Table 13 with regard to steam stripping as a means of trace organic removal.

TABLE 13. APPLICABILITY OF STEAM STRIPPING

Stream	Discussion
Halogenated hydrocarbons	Very volatile - azeotrope with water, two-phase overhead system, stripper bottoms biodegradable. Steam stripping offers possibilities for application to this process effluent.
Aromatic rich effluent from styrene plants	Volatile - azeotropic with water, two-phase overhead system, stripper bottoms organic free. Steam stripping should be effective for this process effluent.
Aromatic amines and polyols	Extremely water soluble - The number of various organics present in this waste water would not permit successful aromatic steam stripping.

Monochem Soot Carbon

In the manufacture of acetylene utilizing methane as raw material, a by-product soot results. This soot is in the 25 to 150 micron range and appears as an emulsified slurry in final form from the process. Preliminary investigations indicated that this material could be dried and activated to yield a commerically acceptable product. This soot carbon was developed and compared with the commercial activated carbons for its applicability to removal of organics from the process effluents.

Ozonation

The original rationale for using ozone as an oxidizing agent was that the halogenated hydrocarbons and aromatics exhibited increased biological activity with high residuals of total organic carbon. For example, toluene itself is not very biodegradable; however, its oxidized counterpart, benzoic acid, is readily biodegradable. Thus, partial oxidation of an aromatic in a process effluent, prior to a biological treatment, would improve its biodegradability. The same technique could be used for halogenated hydrocarbons, polyols, and aromatic amines.

SECTION 5

ACTIVATED CARBON ADSORPTION

Based on the characterizations of the process effluents and inspection of the individual contaminants, the wastewaters were divided into three main subgroups.

Number of Streams	Manufacturing Wastewater Source	Major Organic Contaminant
17	Production of ethylene dichloride, perchloroethylene, and 1,1,1-trichloroethane	Halogenated hydrocarbons
2	Polyols and methycellulose	Polyhydric alcohols
4	Ethylbenzene, styrene, toluene diisocyanate and other process quench waters	Aromatics, organic oxides, or aromatic amines

Past experience indicated that halogenated hydrocarbons, aromatics, and organic amines should be readily adsorbed by activated carbon. Polyols and polyhydric alcohols should not be very adsorbable due to their high molecular weights. Previous studies also indicated they were readily biodegradable, so that best available technology would tend to favor treatment schemes other than carbon adsorption for these two process effluents.

With this in mind, it was decided to investigate process effluents containing chlorinated hydrocarbons, aromatics, and aromatic amines. Since wastewaters contaminated with chlorinated hydrocarbons made up the bulk of the process effluents, it was desirable to include several different industry sources. Wastewaters from three manufacturing processes for chlorinated organics were selected.

Stream number	Type of contaminant
041-A	Chlorinated hydrocarbons
161-A	Chlorinated hydrocarbons
221-A	Chlorinated hydrocarbons
351-A	Aromatic hydrocarbons
231-A	Aromatic amines

LABORATORY PROGRAM

Introduction

After the process effluents were selected, the laboratory procedure for implementation of this phase of the program was set up. The ultimate aim of the project was to field test two adsorption demonstration units at several selected sites. An indepth laboratory program was devised to yield the information desired for the subsequent field work.

The process effluents have been selected. Standard commercial activated carbons were chosen for comparative purposes. The initial step in the evaluation of an activated carbon was to determine its adsorption capacity for the contaminants present in the wastewaters. This was done by applying Freundlich isotherm studies to each carbon tested.

Effluent Isotherms Monitored for Halogenated Hydrocarbon Residuals

Ethylene dichloride (EDC) adsorption isotherms were obtained for streams 041A, 221A, and 161A. Westvaco (WVG) Calgon, WITCO, and Barneby Cheney carbons were used for streams 041A and 221A. Only WVG carbon was used for stream 161A. The other carbons were dropped because WVG carbon gave the best results in the previous tests. Although other organics were known to be present in these wastewaters, EDC was the chlorinated hydrocarbon most prevalent. Thus, the adsorption characteristics could be interpreted with the determination of this compound. Effluent isotherms have been plotted for streams 041A, 221A, and 161A and are included in the Appendix. The data are summarized in Tables 14 and 15.

Observations--

1. Stream 041A: Calgon (FS-400) exhibited the highest adsorption capacity for EDC, followed by Barneby-Cheney (BCNB-9377), WITCO, and Westvaco.

2. Stream 221A: WITCO, Westvaco, and Calgon were effective in this order for EDC removal.

3. Stream 161A: Calgon exhibited less adsorption capacity than Westvaco over a narrower range of EDC residual concentration.

4. A carbon having the highest adsorption capacity in the higher range of residual EDC concentration did not necessarily exhibit highest adsorption capacity in the lower range of residual EDC concentration.

Monochem Activated Soot Carbon Isotherms

Included in this program was a waste stream emanating from an acetylene manufacturing process, which forms acetylene from the cracking of natural gas. A very fine carbon black is formed as a by-product and is removed from the product gas by a water quench. This water carries the carbon black "soot carbon" to a separator station where it is dewatered and burned.

TABLE 14. ADSORPTION CAPACITY OF ACTIVATED CARBONS FOR REMOVAL OF ETHYLENE DICHLORIDE

Stream Number	Filtrasorb 400 (gms/gm Carbon)	Westvaco 12 X 14 (gms/gm Carbon)	Witco (gms/gm Carbon)	Barneby NB3377 (gms/gm Carbon)	Monochem Soot Carbon (gms/gm Carbon)
Carbon required for a residual of 10 mg/1 EDC					
041A	0.85	1.0	0.55	0.47	0.13
221A	0.55	1.25	0.60	-	0.125
Carbon required for a residual of 0.1 mg/1 EDC					
041A	0.13	0.0126	0.07	0.12	
221A	0.055	0.055	0.10	-	
161A	0.014	0.0145	-	-	

TABLE 15. ADSORPTION CAPACITY OF ACTIVATED CARBONS FOR REMOVAL OF TOC

Stream Number	Filtersorb 400 (gms/gm Carbon)	Westvaco 12 X 14 (gms/gm Carbon)	Witco (gms/gm Carbon)	Barneby Cheney (gms/gm Carbon)	Monochem Soot Carbon (gms/gm Carbon)
Carbon required for a residual of 0.5 mg/1 TOC					
041A	0.35	0.062	0.052	0.42	-
221A	0.65	0.7	0.6		0.3
Carbon required for a residual of 50 mg/liter					
231A	100	150	-	15	25
351A	25	20		7.0	7.0

A development program was established to formulate an activated carbon from this waste material. The soot carbon was activated by Envirotech in California. The activation temperature used was between 870°C and 925°C with a steam blanket.

The granular activated carbon sample was received at GSRI in the form of a very thick slurry in water. It had a considerable amount of carbon fines in it. These fines were washed off with copious quantities of water. The granules were oven dried at 200°C for approximately 48 hr. The dried carbon granules were used to make adsorption isotherm and breakthrough measurements.

Effluent Isotherms Monitored for Total Carbon Residuals

In an attempt to define the composition of effluent waters after treatment with activated carbon, adsorption isotherms were generated using total carbon (TC) as a measure of concentration for streams 041A and 221A. Filtrasorb-400, WVG, WITCO, Barneby-Cheney BCNB-9377, and varieties of activated soot carbon were used. Standard experimental procedure was followed to obtain the adsorption isotherms.

Observations--

1. WVG was the best among the carbons evaluated for total carbon removal of streams 041A and 221A.

2. Activated carbon that adsorbs maximum EDC does not necessarily adsorb maximum TC.

3. Stream 041A lent itself to adsorption with commercial carbons better than stream 221A.

4. TC adsorption capacity of the activated soot carbon was less than 50 percent of the adsorption capacity of commercial carbons.

Effluent Isotherms for Streams 231A and 351A

Two streams from other processes were investigated as part of the preliminary studies. These two streams were produced by an ethyl benzene-styrene plant (351A) and a toluene diisocyanate plant (231A).

Stream 351A contained predominantly benzene and ethyl benzene and is basic. This stream was treated with various activated carbons. Experimental data indicate that Westvaco Nuchar carbon yielded an isotherm that would have an adsorption capacity of 0.285 g TOC/kg carbon. All other carbons tested would leave a residual TOC concentration of 4 to 30 mg/l; only the Nuchar carbon appears to treat the stream effectively. Stream 231A contained water-soluble organic compounds from a process making toluene diisocyanate and toluene diamine compounds. The wastewater was too dilute to permit compound identification. However, Westvaco and Filtrasorb-400 activated carbon appeared to offer the best removal characteristics when tested for the reduction of TOC as the gross parameter.

Dynamic Tests for Breakthrough Evaluations

Estimation of mass transfer parameters for column design and comparison of performance of different carbons under dynamic conditions is accomplished by breakthrough measurements. A plot showing the relationship between the cumulative volume of liquid passed through a carbon column and the effluent concentration of the component being removed is termed "breakthrough" curve. For most adsorption operations in water and wastewater treatment, breakthrough curves exhibit a characteristic S shape, but with a varying degree of steepness. A steep curve indicates a high rate of adsorption; a short, steep curve indicates a high rate of adsorption, but also a short column service life. Figure 6 shows typical breakthrough curves. Obviously, Column A will have a shorter service life than Column B.

A specially fabricated glass apparatus provided a constant liquid head to the three columns (made of chromatographic tubes with 20 mm ID and 450 mm length). Feed flow rates were varied and accurately controlled by the precision stopcock on each of the tubes. The schematic of the apparatus is shown in Figure 7. Waste stream samples were analyzed on a gas chromatograph for EDC and on a total carbon analyzer for total carbon.

Five combinations of carbons and waste streams were used in establishing the dynamics expected in the field trials. Two characteristic streams were used. The sample of 041A used for these experiments was high in chlorinated hydrocarbons (approximately 8,000 mg/l), highly alkaline, and showed a total carbon by the Beckman method of approximately 1,200 mg/l. Stream 221A had a total chlorinated hydrocarbon content of approximately 12,000 mg/l and was acidic. The total carbon level of about 6,000 mg/l clearly indicated the presence of nonchlorinated hydrocarbons.

Three carbons were used during the trials: (1) WVG carbon, which had shown a high equilibrium adsorption of EDC and total carbon previously, (2) Filtrasorb-400, which had also shown a high adsorptive capacity, and (3) activated soot carbon treated in the laboratory to a medium level of activation. The limited amount of soot carbon precluded carrying out the complete test program with this carbon.

For each combination, three breakthrough curves were generated at three different flow rates denoted by L (low), M (medium) and H (high). The range of flow rate were expressed as liters per square meter of activated carbon.

L: 0.57 l/m^2 to 1.13 l/m^2
M: 1.13 l/m^2 to 1.98 l/m^2
H: 1.98 l/m^2 to 2.83 l/m^2

For stream 041A, the reduction of EDC was accomplished equally well by Filtrasorb-400 and WVG. However, bed life of the soot carbon sample studied would be only 40 to 50 percent as long as that of the two commercial carbons. The Filtrasorb-400 appeared to have less sensitivity to flow rates that the WVG in the range studied. The soot carbon did not show any flow effects.

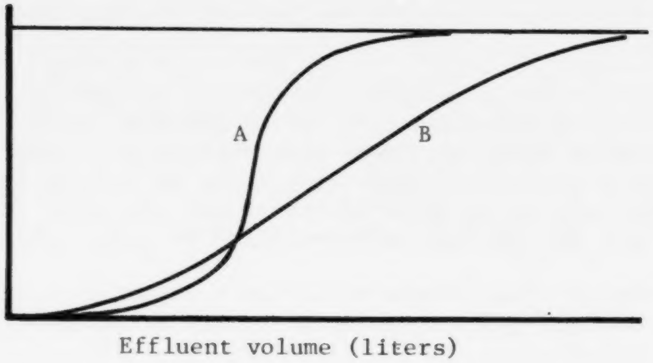
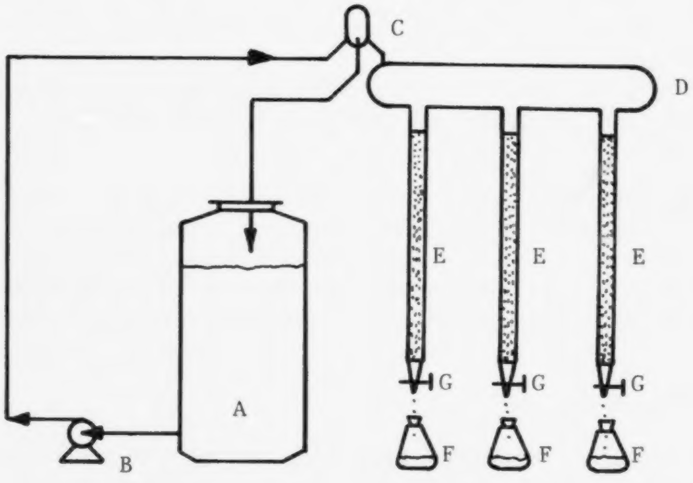


Figure 6. Typical breakthrough curves.



A - Feed reservoir
B - Feed pump
C - Constant level device
D - Feed distribution manifold
E - Carbon columns
F - Sample flasks
G - Stopcocks

Figure 7. Laboratory continuous carbon adsorption apparatus.

For stream 221A, the minimum total carbon level obtainable in the effluent from carbon column is about 300 mg/l independent of the type of carbon used. Highest capacity for the solutes in this stream was shown by WVG, followed by Filtrasorb-400 and soot carbon. Little sensitivity to the flow rates was found for the soot carbon. The data indicated that a species other than chlorinated hydrocarbons was present and was poorly adsorbed by carbons.

The capacity of both commercial carbons for stream 221A was nearly the same, and was significantly less than for stream 041A. The capacity of the activated soot carbon again was lower than that of the commercial carbons. With this stream, higher flow rates bring about an earlier breakthrough. While high acidity may be expected to reduce the available adsorption sites of the carbon, this has not been substantiated by reductions in acidity.

The reduction of total carbon in effluent stream 221A was inefficient with WVG and Filtrasorb-400. The removal of the nonchlorinated hydrocarbons will have to be achieved by some other method.

Observations--

1. At 6000 mg/l, EDC, adsorption capacity of the activated soot carbon was no greater than 55 percent of the adsorption capacity of commercial activated carbons. However, at 1000 mg/l EDC, the adsorption capacity of the former was approximately 75 percent of that of commercial activated carbon.

2. A better EDC adsorption capacity for stream 221A than for stream 041A with activated soot carbon was observed.

3. An improvement of 20 to 25 percent was observed in the adsorption capacity of EDC over the two previous batches (#79 and #104) of activated soot carbon.

4. The breakthrough profile for stream 041A indicated a higher service life for stream 041A than for stream 221A. The concentration gradient of the organics in the carbon bed indicated the absorption capacity of the carbon would be better utilized before the concentration of the organics in the outlet exceeded specified limits.

Regeneration of Spent Activated Carbon with Stream

Regeneration and reuse of spent activated carbon is one of the most important factors in determining the economic feasibility of the activated carbon adsorption process. Carbon beds have to be regenerated after their product exceeds a predetermined level of acceptable impurities.

Regenerability--

Five spent carbon samples were regenerated with 1 atm steam for a period of 15 min. The adsorptivity of the regenerated samples of carbon was compared with the fresh carbon samples. For the comparison, accurately weighed 2 g samples of the fresh and regenerated carbons were added to 100 ml waste stream in a glass stoppered flask. After equilibrating these samples for 24 hours, fractional reduction of EDC for the regenerated and the fresh carbon was determined. The regeneration efficiency E was computed as:

$$\% \text{ E} = \frac{\text{FR for 2 g regenerated carbon}}{\text{FR for 2 g fresh carbon}} \times 100$$

where FR is the fractional reduction of solute.

Results with EDC and TC as measures of concentration are listed in Tables 16 and 17.

TABLE 16. REGENERATION EFFICIENCY - EDC

Stream	Carbon Name	Fraction Reduced With Fresh Carbon	Fraction Reduced with Regenerated Carbon	Regeneration Efficiency (Percent E)
041A	WVG	0.945	0.93	98
221A	WVG	0.64	0.60	94
041A	Filtrasorb	0.94	0.92	98
221A	Filtrasorb	0.65	0.59	91
041A	Monochem	0.66	0.57	93

Weight of Carbon: 2.00 g
Volume of Waste Stream: 100 ml
Solute: EDC (11,000 mg/l)

The data of Table 17 were obtained to check the conclusions based on EDC measurements. Both sets of data show an excellent potential for low pressure steam regeneration of the spent activated carbon *in situ*. Regeneration efficiencies were generally lower on stream 221A than on stream 041A.

TABLE 17. REGENERATION EFFICIENCY - TC

Stream Number	Carbon Name	Fraction Reduced With Fresh Carbon	Fraction Reduced With Regenerated Carbon	Regeneration Efficiency (Percent E)
221A	Westvaco	0.135	0.101	75
041A	Filtrasorb	0.092	0.09	98

Weight of Carbon: 2.00 g
Volume of Waste Stream: 100 ml
Solute: TC
Solute Concentration: #041A - 950 mg/l
#221A - 5200 mg/l

Regeneration Time--

To determine the effect of regeneration time on the efficiency of regeneration, approximately 200 g of Filtrasorb-400 was equilibrated with 3 liters of stream 221A for a period of 16 hr. The EDC loading on the carbon was determined by measuring fractional EDC reduction in the residual 221A solution. The 221A solution was then drained and the EDC loaded carbon was washed three or four times with 2 liters of tap water. The carbon was divided into two equal fractions of about 100 g each. At 1 atm steam pressure, each fraction was regenerated for the time indicated. Regeneration efficiencies were determined. Results are listed in Table 18.

TABLE 18. VARIATION OF REGENERATION TIME

Regeneration Time	Fraction Reduced With Fresh Carbon	Fraction Reduced With Regeneration Carbon	Regeneration Efficiency (Percent E)
2 Minutes	0.76	0.70	92
5 Minutes	0.76	0.71	93
15 Minutes	0.65	0.59	91

Carbon: Filtrasorb-400
Waste Stream: 221A
Solute: EDC

Repeated Regenerations--

Preliminary tests indicate that it is technically feasible to regenerate the carbon that is subject to loading by streams 041A and 221A. However, these tests were limited to single regeneration. To study the effect of repeated regenerations on the adsorption capacity of the spent reactivation carbon, EDC loading on carbon and the regeneration efficiency were determined after several regenerations at 1 atm. A quantity of 100 g of Filtrasorb-400 was equilibrated overnight with 2 liters of 221A solution. The loaded carbon was washed several times with tap water and was regenerated with 1 atm steam for 5 min. This procedure was repeated four times on the same carbon sample. After five regenerations, EDC loading on the regenerated sample was 0.186 g EDC/g carbon, as compared to 0.2 g EDC/g fresh carbon. The regeneration efficiency was 93 percent.

DEMONSTRATION UNIT PROGRAM

Introduction

After the laboratory evaluation of activated carbon for removing trace organics from selected process effluents, an on-site field evaluation was conducted. The two activated carbon adsorption units for use in the field testing portion had the following items of equipment.

1. Four 127 mm I.D. by 1828.8 mm long plastic columns connected in series with 12.7 mm polypropylene tubing. The initial columns were made of Plexiglas. These columns were subsequently replaced with fiberglass and polypropylene because of the solvent effects of the ethylene dichloride contaminated wastewaters.

2. An A-frame rack on which the columns were suspended. The A-frame was built of 38 mm nominal pipe with welded assembly.

3. Variable speed pump: Maximum discharge pressure 1.36 atm. Pump speed and liquid flow rate were controlled by motor drive and pump pulley sizes. The pulley provided flow rates ranging from 1.48 to 3.69 l/min. The pump was supplied with Viton® tubing with an expected lifetime of 10 hr at flow rates 3.42 to 3.8 l/min. Calibration curves were provided for the various pulley sizes.

4. Electric motor: 110 V. A.C. 1/4 HP T.E.F.C. motor for the pump.

5. Temperature and pH monitor: A flow-through chamber containing pH and temperature sensor provided with a dual channel "Rustrak" recorder.

The columns were prepared by placing a double layer of fiberglass window screen in the bottom of each column followed by a 10 cm to 15 cm layer of pea gravel. A heavy slurry of water and carbon (pre-soaked 24 hr to deaerate the carbon) was then added to the columns to a desired height. The columns were backwashed when the gauge pressure on the lead column was 1.3 atm or more. The backwash flow was 15.2 l/min (this corresponds to a 30 to 50 percent bed expansion).

Process Effluent Selections for Demonstration Unit Evaluations

The demonstration units were operated at three process effluent locations: (a) process effluent stream 221A, (b) process effluent stream 041A, and (c) process effluent stream 081A. Three commercial carbons and the Monochem activated soot carbon were evaluated.

Each pilot unit was operated at approximately 1.0 l/min during the testing. This operation provided a screening for selecting the best of the commercial carbons to compare with the activated soot carbon. Test duration depended on the adsorption rate of each carbon relative to each stream.

After the best carbon had been selected, a series of tests was conducted to determine design data for that carbon, as well as the Monochem carbon. These tests consisted of breakthrough runs at various flow rates and organic loading rates. Hydrodynamic data were also collected to ascertain flow and pressure drop characteristics of the pilot unit.

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PROCESS EFFLUENT STREAM 221A

Capacity and Breakthrough Data

The first field tests were made on process effluent stream 221A. Four commercial carbons were evaluated for breakthrough and adsorptive capacity limitations. However, the process influents for this series of tests varied considerably during the experimental operations, and breakthrough points were inconclusive.

The effectiveness of activated carbon for stream 221A was initially measured by total organics adsorbed. It was recognized that other organics might be present which were not being adsorbed. Since removal of organics would be indicated by a reduction in oxygen demand, total carbon and total oxygen demand (TOD) measurements on the influent to and effluent from the carbon columns were incorporated as an indication of the carbon needed to remove total contaminants present.

When a comparison was made between the analyses for organics, TC, and TOD, the activated carbon appeared to allow some of the organic contaminants to pass through because some variation in inlet flow occurred during the field tests. This variable flow caused the loading on the carbon to change, thus affecting the concentration of organics in the column effluent. Most of the data obtained for the organic components in the process effluent indicated a definite breakthrough for this parameter.

In some instances, the gas chromatograph (GC) detected low minimum chlorinated hydrocarbons, although the TC and TOD data indicated considerable contaminants passing through the adsorption unit.

The production unit generating effluent stream 221A utilizes the oxychlor process. In the reaction of ethylene, chlorine, oxygen, and recycled higher chlorinated hydrocarbons, side reactions occur which produce trace components. These trace organics include chloroacetaldehyde (chloral-trichloroacetaldehyde), aldehydes, hydroxy chlorinated hydrocarbons, and other related compounds.

Chloral and formic acid are two of the most prevalent side reaction trace components generated during the oxychlor reaction. Both of these trace compounds are biodegradable. A central biotreatment system would remove chloral and formic acid.

Effects of Flow Rate on Adsorption Capacity

As expected, the capacity of the carbon to remove organic contaminants from the wastewaters varied with the rate of flow for a consistent amount of contaminants in the feed. Certain organic contaminants, such as chloral, which are water soluble and form hydrates, affect the adsorption capacity at different flow rates. These data are summarized in Tables 19 and 20.

TABLE 19. EFFECTS OF FLOW RATE ON ADSORPTION CAPACITY FOR STREAM 221A
(Kg Adsorbed/Kg Carbon)

Total Organics by Gas Chromatography

1.64 l/min		2.27 l/min		3.41 l/min	
Feed (kg)	Adsorption (kg/kg carbon)	Feed (kg)	Adsorption (kg/kg carbon)	Feed (kg)	Adsorption (kg/kg carbon)
0.071	0.0023	0.277	0.0097	6.029	0.263
0.982	0.0317	1.516	0.0531	10.984	0.425
2.257	0.0728	2.980	0.1043	12.297	0.358
2.958	0.0954	5.057	0.1771	17.706	0.489
3.961	0.1277	8.124	0.2844	23.429	0.521
5.322	0.1716	12.222	0.4005	31.775	0.435
7.042	0.2270	15.241	0.4235		
8.146	0.2626	18.731	0.4241		
9.181	0.2924				
10.036	0.3048				

Total Organics by TOD

1.64 l/min		2.27 l/min		3.41 l/min	
Feed (kg)	Adsorption (kg/kg carbon)	Feed (kg)	Adsorption (kg/kg carbon)	Feed (kg)	Adsorption (kg/kg carbon)
0.157	0.0046	0.150	0.0052	1.791	0.072
5.142	0.0156	1.109	0.0388	3.414	0.122
1.296	0.0348	1.658	0.0486	4.042	0.123
1.691	0.0450	2.388	0.0663	6.222	0.159
2.245	0.0596	3.208	0.0717	8.004	-
2.731	0.0695	4.576	0.0824	10.00	-
3.342	0.0823	5.374	0.0778		
4.043	0.0989	6.884	0.0979		
4.333	0.1040				
4.942	0.1041				

TABLE 20. ANALYSIS OF ADSORPTION DEMONSTRATION UNIT OPERATION BY INDIVIDUAL ORGANIC COMPONENT FOR STREAM 221A

	Test One Carbon: Westvaco Stream: 221A Flow: 1.1 l/min Loading: 0.74 l/cm^2/min Columns: 15 x 150 cm Volume: 64.8 liters		Test Two Carbon: Westvaco Stream: 221A Flow: 1.9 l/min Loading: 1.23 l/cm^{2}min Columns: 15 x 150 cm Volume: 64.8 liters		Test Three Carbon: Westvaco Stream: 221A Flow: 2.85 l/min Loading: 1.84 l/m^2/min Columns: 15 x 150 cm Volume: 64.8 liters		Test Four Carbon: Filtrasorb 300 Stream: 221A Flow: 1.1 l/min Loading: 0.71 l/m^2/min Columns: 15 x 150 cm Volume: 64.8 liters	
Organic Component in Influent and Effluent	Total Organics To Columns Before Breakthrough (mg)	Organics Adsorbed Before Breakthrough (mg)	Total Organic To columns Before Breakthrough (mg)	Amount Adsorbed Before Breakthrough (mg)	Total Organics To columns Before Breakthrough (mg)	Amount Adsorbed Before Breakthrough (mg)	Total Organics To columns Before Breakthrough (mg)	Amount Adsorbed Before Breakthrough (mg)
Ethyl Chloride	4000	4000	585	585	992	992	1034	1034
Vinyl Chloride	224	224	6829	6829	182	182	31	31
Vinylidene Chloride	0	0	0	0	898	NB	19	NB
Trans-Dichloroethylene	0	0	0	0	0	0	0	0
1,1-Dichloroethane	2944	NB	13357	NB	5250	5250	2024	NB
Chloroform	1255	NB	13401	NB	2254	NB	1391	NB
Ethylene Dichloride	51100	51100	155743	155743	69369	69369	65494	65494
1,1,1-Trichloroethane	555	NB	1726	NB	-	-	312	NB
1,1,2-Trichloroethane	2530	NB	2151	NB	3369	NB	463	NB
Chloral Hydrate	51000	51000	18459	18459	3920	3920	-	-
Chloral			102600	102600	63612	63612	-	-
Propylene Dichloride			4155	NB	1318	NB	-	-

NB = No Breakthrough

Effectiveness of Activated Carbon on Removing all Chlorinated Hydrocarbons

As discussed in the preceding section, the effectiveness of activated carbon in removing the refractory chlorinated hydrocarbons was determined by measuring the removal of total organics, total carbon, and total oxygen demand in both the influent and effluent of the adsorption system. The influent and effluent were also monitored to study the selectiveness of the removal of specific organics from the process effluent. The monitoring for the specific chlorinated hydrocarbon was done by gas chromatography using a flame ionization tester. This GC method determined all of the chlorinated hydrocarbons quantitatively.

Activated carbon showed an excellent capacity for removing trace levels of chlorinated hydrocarbons. Chloral and chloral hydrates did not adsorb as readily as did the chlorinated hydrocarbons. When effluent samples contained chloral and chloral hydrates in concentrations as great as EDC, these streams exhibited the least adsorptive characteristics and showed breakthrough about the same time as the ethylene dichloride.

Regeneration Results with the Shirco Infrared Furnace--

Regeneration of activated carbon utilized in stream 221A involved six samples of four commercial carbons (Tables 21 and 22). After six sample runs, operation was shut down because of the condition of the adsorption columns. The chlorinated organics present in the wastewater attacked the Plexiglas walls and produced crazed cracking. The tubes were replaced with polypropylene reinforced with carbon black.

Since the test activated carbon was regenerated off-site, it was stored in metal drums for transport. Minimum sealing was maintained since the carbon would be heated for regeneration. Storage and weathering prior to regeneration led to the removal of some 80 to 90 percent of the volatile chlorinated hydrocarbons. Data at saturation showed from 0.2 to 0.45 kg of adsorbed organics/kg activated carbon, while the analysis prior to regeneration indicated only 0.01 to 0.08 kg organics present/kg activated carbon.

Results of the regeneration tests on all four commercial carbons are shown in Table 21. Several samples had become dry through storage and were run as received. Initially, a low temperature and long residence time were utilized for regeneration. One test was made at a short residence time and a higher temperature to evaluate these variables. The first run indicated that residence time and condition of the carbon (wet or dry) had little effect on the regeneration results, but that higher temperatures were needed for complete regeneration. A second run was made to study the effects of higher temperature on regeneration. These results are presented in Table 22.

Since the earlier studies on stream 221A had shown Westvaco WVG to be the best activated carbon in terms of organics removed per kilogram of carbon, it was decided to run the iodine numbers for this carbon.

TABLE 21. REGENERATION OF SPENT ACTIVATED CARBON - RUN NO. 1

Activated Carbon	Condition	Residence Time (Minutes)	Output (kg/hr)	Furnace Temperature °C Lamp Section 1 & 2	Furnace Temperature °C Lamp Section 3 & 4	Kg of Organics/Kg of AC* Initial	Kg of Organics/Kg of AC* First Run
Filtrasorb-300	Wet	18-20	45.5	371-427	677-732	0.0137	0.0064
Filtrasorb-400	Wet	10-12	90.8	399-454	732-788	0.0867	0.0436
Witco 718	Wet	10-12	90.8	399-454	732-788	0.0455	0.0232
Westvaco WVG #1**	Dry	10-12	90.8	399-454	732-788	0.0312	0.0160
Westvaco WVG #2**	Dry	10-12	90.8	399-454	732-788	0.0349	0.0214
Westvaco WVG #3**	Dry	10-12	90.8	399-454	732-788	0.0517	0.0305

*Analyses were made on a hexane extract of the activated carbon granules.

**Refers to flow rate of Stream 221A while this activated carbon was in the Number 2 unit: Number 1, lowest; Number 2, medium; Number 3, highest.

TABLE 22. REGENERATION OF ACTIVATED CARBON - RUN NO. 1

Activated Carbon	Conditions	Residence Time (Minutes)	Output (kg/hr)	Furnace Temperature °C Lamp Section 1 & 2	Furnace Temperature °C Lamp Section 3 & 4	Kg of Organics/Kg of AC Initial	Kg of Organics/Kg of AC First Run
Filtrasorb-300	Dry	6-7	300	816-927	816-1066	0.0137	0.00018
Filtrasorb-400	Dry	6-7	300	760-899	927-954	0.0867	0.0041
Witco 718	Wet	6-7	300	704-816	760-927	0.0455	0.00102
Westvaco WVG #1	Dry	6-7	300	760-899	927-982	0.0312	0.00060
Westvaco WVG #2	Wet	6-7	300	704-899	954-982	0.0349	0.00029
Westvaco WVG #3	Wet	6-7	300	760-899	899-927	0.0517	0.00070

	Iodine Number
WVG Carbon as Received	1165
WVG #1 after regeneration at 927-982°C	1058
WVG #2 after regeneration at 954-982°C	993
WVG #3 after regeneration at 889-954°C	838

The difference in iodine numbers was not reflected in the organics removed.

Retesting of Westvaco Activated Carbon

Stream 221A was re-evaluated on a new batch of WVG activated carbon on an adsorption-regeneration cycle. The demonstration unit was repacked with a fresh batch of WVG carbon. After saturation, an adsorption capacity of 0.34 kg organics/kg carbon was observed (Tables 23 and 24). This was almost identical to the initial test where capacity was 0.33 kg organics/kg carbon.

The saturated carbon was transported to the site of the Shirco furnace in polyethylene drums. The regeneration conditions for this batch were approximately the same as those used for the earlier batches of carbon. Conditions were as follows:

Carbon Sample	Wet Westvaco
Furnace Temperature	
Lamp Sections 1 and 2	496°C Average
Lamp Sections 3 and 4	737.5°C Average
Atmosphere	Nitrogen
Residence Time	10 Minutes

The iodine number of the fresh WVG was 1150. After regeneration, it was 1056. The amount of adsorbed organics determined by a GC analysis of a perchloroethylene extract of the carbon was 0.138 kg organics/kg carbon before regeneration, and 0.0008 kg organics/kg of carbon after regeneration.

These data indicate much better regeneration characteristics than the previous run. However, it must be realized that small quantities of carbon were being handled (22.3 kg/case) and that small losses are easily magnified in the recycle process.

PROCESS EFFLUENT 041A

Introduction

This process effluent was selected for demonstration unit evaluation because it was similar in organic contaminants to stream 221A; however, the pH of stream 041A was 12, compared to pH 1 for stream 221A. The procedure used to develop the demonstration unit data was much the same as that followed for stream 221A.

TABLE 23. ADSORPTION CAPACITY DATA FROM BREAKTHROUGH STUDY OF STREAM 221A

		Influent Number Kg Organics		Effluent Number Kg Organics					
Hour	Liters	Period	Total	Period	Total	Kg Adsorbed	Percent Adsorbed	Cumulative Kg Adsorbed	Cumulative Number Kg of Organics/ Kg/Carbon
0-2	228	.745	.745	0.000	0.000	.745	100.000	.745	0.02024
2-24	2120	4.075	4.819	0.000	0.000	4.819	100.000	4.819	0.1310
24-49	5267	4.731	8.550	0.301	0.301	4.430	93.63	9.250	0.2515
49-59	6680	4.264	13.815	0.740	1.041	3.222	75.56	12.482	.3391
59-72	8460	4.433	18.248	4.380	5.421	0.053	0.103	12.525	.3405

TABLE 24. STUDY OF THE ADSORPTION CAPACITY OF REGENERATED WESTVACO-WVG COMPARISON OF THE EFFLUENT AND INFLUENT FOR STREAM 221A

Date	Water Sample[a]	COD (mg/1)	TOD (mg/1)	TOC (mg/1)	Total Organics (mg/1)	Major Organics				Acidity (mg/1)
						EDC[b]	CH[c]	EC[d]	DCE[e]	
7/22	1-01-I	1,192	1,759	724	2,253	952	1,086	387	40	10,550
7/22	1-11-E	446	264	76	0	0	0	0	0	8,750
7/22	1-21-E	225	136	40	0	0	0	0	0	1,300
7/23	1-02-I	995	1,804	627	2,420	917	1,172	105	79	10,150
7/23	1-12-E	562	624	437	0	0	0	0	0	10,400
7/23	1-22-E	512	460	347	0	0	0	0	0	10,000
7/24	1-03-I	1,554	1,716	567	2,229	963	1,037	59	78	25,200
7/24	1-13-E	1,394	1,812	614	2,220	756	1,250	152	45	3,600
7/24	1-23-E	1,166	1,105	962	1,553	167	1,170	190	8	19,000
	2-01-I	1,110	2,392	663	4,180	3,019	132	327	305	4,260
	2-11-E	1,138	477	297	0	0	0	0	0	30,500
	2-21-E	1,549	1,198	588	607	177	191	239	0	45,100
	2-02-I	1,525	3,638	640	2,500	1,274	994	128	193	4,200
	2-12-E	1,232	585	394	0	0	0	0	0	20,400
	2-22-E	898	620	271	263	78	122	63	0	19,500

[a] 1st number designates run; 2nd, column #; 3rd, sample #.
The letters I and E stand for influent and effluent.

[b] Ethylene Dichloride.

[c] Chloral Hydrate.

[d] Ethyl Chloride.

[e] 1-1-Dichloroethane.

1. Review of the activated carbon laboratory equilibrium data.
2. Demonstration unit operation.
3. *In-situ* steam regeneration.
4. Breakthrough data.
5. Further demonstration unit tests.

Location and Setup of Demonstration Unit

Stream 041A was first evaluated to determine the removal of trace chlorinated hydrocarbons by carbon adsorption. Based on preliminary laboratory data, it was decided to use WVG, Filtrasorb, and Witco activated carbon for this study. The stream was pumped through three carbon beds in series at selected flows. Regeneration evaluations were made utilizing steam passed through the carbon beds *in situ*.

Demonstration Unit Operation

The demonstration unit was set up adjacent to the production unit, and the column was packed with the first carbon to be tested, WVG. These first test results are represented as run number one of Table 25. The second run was initiated with Filtrasorb-400 charged to the unit. A high flow rate (3.4 l/min) was used for this second run and resulted in a relatively quick breakthrough as indicated by EDC measurements. The first three columns were saturated in less than eight hours. The breakthrough was not followed through each column since it occurred before the first set of samples was completely analyzed. The capacity calculations listed in Table 25 for the second run were based on three columns and resulted in high values when compared with subsequent data.

The Witco 718 carbon, run number three (Table 25), appeared to be the best carbon tested based on adsorption capacity before breakthrough of EDC. This carbon removed 0.35 kg EDC/kg carbon. Unfortunately, this represents one set of data with no confirmation.

The remaining capacity runs were made with the WVG carbon. Runs four and five resulted in adsorption capacities of 123 g EDC/liter carbon, or 0.28 kg EDC/kg carbon.

In Situ Steam Regeneration

An important part of the carbon adsorption process is the regeneration and neutralization of the carbon after it has become saturated. The conventional regeneration technique is to remove the carbon and regenerate it, burning off the adsorbed impurities in a multihearth furnace. After this burnoff, the carbon is cooled and replaced in the original reactor for the next cycle of operation.

TABLE 25. SUMMARY OF CARBON ADSORPTION FIELD TRIALS ON STREAM 041A

Run Number	carbon Type	Flow Rate 1/min	Total Run Time Hours	No of Columns	Height (m)	Weight (kg)	Volume liters	Influent mg/1	Effluent mg/1	EDC Retained in Bed (kg)	Carbon Adsorption Capacity	
											(kg EDC) / 1 Carbon	(kg EDC) / kg Carbon
1	WVG	0.95	16-24	1	1.82	5.66	13.44	3600	-	3.45-4.90	0.26-0.36	0.6-0.8
2	Filtrasorb 400	0.76	3	3	3.95	16.6	39.14	3662	0	5.72	9.2	0.33
3	Witco 718	0.95	100	5	6.87	61.4	124.8	3508	<14	21.5	0.17	0.35
4	WVG	0.76	38	3	2.01	15.4	36.1	2080	<50	5.26-6.12	0.11-0.12	0.25-0.29
5	WVG	0.95	48	3	3.40	27.1	28.32	2750	<98	7.76	0.12	0.28
6	WVG	0.95	72	5	5.56	44.4	103.7	3042	<50	125.8	0.12	0.28
7	WVG	0.76	24	1	0.14	9.71	22	2300	-	-	-	-
8	WVG	0.76	24	1	1.21	9.71	22	2350	-	-	-	-
9	WVG	0.76	26	1	1.21	9.71	22	1800	-	-	-	-
10	WVG	0.76	23	1	1.21	9.71	22	2817	249 Composite	2.72	0.12	0.28
11	WVG	0.76	48	1	1.21	9.71	22	-	-	-	-	-
12	WVG	0.76	48	1	1.21	9.71	22	-	-	-	-	-
13	WVG	0.76	48	1	1.21	9.71	22	-	-	-	-	-
14	WVG	0.76	120	1	1.21	9.71	22	-	-	-	-	-
15	WVG	0.76	24	1	1.21	9.71	22	-	-	-	-	-
16	WVG	0.95	17.5	1	1.21	9.71	22	3067	80 Composite	2.72	0.12	0.28

An undesirable aspect of thermal regeneration of carbons saturated with chlorinated organics is that the combusting gases contain hydrogen chloride. The results of solving the effluent problem could be to create an emission problem via this process. Steam regeneration of activated carbons saturated with certain organics has distinct advantages. With steam, it is possible to condense the hot vapors escaping from the reactor outlet. If the stripped organics are immiscible, they can be decanted and returned to the process. If they are soluble, it may be possible to separate them from the condensate by fractionation. In either case, this regeneration technique permits recovery and recycling of the contaminants.

One of the objectives of this program was to evaluate steam regeneration of carbon. Toward this end, provisions were made to steam-strip the carbon after saturation with EDC from the process effluent. The results of these tests (runs six through sixteen) are presented in Table 26. Each run was preceded by up to 24 hours of low pressure steam-stripping.

Runs six, ten, and sixteen were analyzed for EDC. Subsequent testing yielded the same adsorption capacities as did runs four and five, which used fresh carbon.

This experimental work pointed up several salient aspects of the utilization of activated carbon to recover EDC from this process effluent.

1. The carbon bed could be steam-stripped of the EDC in situ.
2. The original capacity of the carbon was completely restored.
3. There was no apparent effect of repeated regeneration on the physical integrity of adsorption capacity of the carbon.
4. After 11 in situ steam regenerations of the same carbon bed, there were no signs of "bed wear."

Breakthrough Data

Each of the adsorption columns was monitored for EDC while evaluating the selected commercial activated carbon installed for the test. Tables 26-30 follow the breakthrough of EDC through each column of the demonstration unit.

Further Demonstration Unit Tests on Stream 041A

Three additional carbon adsorption runs were made on stream 041A. One involved a recheck of the adsorption capacity of Filtrasorb-400, and the other two were studies of the adsorption capacity of new and regenerated Monochem activated carbon.

The waste in stream 041A was composed of about 99 percent by weight of ethylene dichloride. The EDC concentration in the influent and effluent were determined by gas chromatography. Earlier field studies of stream 041A indicated that Filtrasorb-400 and Witco 718 had higher adsorption

TABLE 26. BREAKTHROUGH DATA WITH FILTRASORB-400 (STREAM 041A)

Flow: 3.42 1/min.

Loading: 1.61 1/min^{-}M^{2}

Total Liters	EDC (mg/1) Column						Total Carbon (mg/1) Column						Pressure Drop (atm) Column					
	Feed	1	2	3	4	5	Feed	1	2	3	4	5	Feed	1	2	3	4	5
1640	3662	3446	3766	3409	0	0	1220	1530	1270	1470	320	200	0.612	0.477	0.374	0.136	0.136	0
3276	-	3819	3472	3598	3851	3693	-	1330	1360	1470	1260	1240	2.00	1.80	1.53	1.36	1.34	1.24

TABLE 27. BREAKTHROUGH DATA WITH WITCO 718 (STREAM 041A)

Flow: 0.95 1/min

Loading: 0.45 1/min M^{2}

Total Liters	EDC (mg/1) Column						Total Carbon (mg/1) Column						Pressure Drop (atm) Column					
	Feed	1	2	3	4	5	Feed	1	2	3	4	5	Feed	1	2	3	4	5
170	3508	0.8	4.8	4.6	6.8	1.5	2183	-	-	-	-	-	0	0	0	0	0	0
795	-	1780	0.9	0.7	1.7	0.4	-	484	387	-	-	-	0	0	0	0	0	0
1389	3409	2588	61.9	13.9	7.3	4.0	2183	1478	-	-	-	-	0.14	0	0	0	0	0
1643	-	2999	7.4	7.9	5.7	10.7	-	1934	497	-	-	-	0.14	0	0	0	0	0
2188	-	4135	7.6	6.5	6.8	3.6	-	1022	359	553	499	-	-	0	0	0	0	0
2612	3560	3251	1570	17.5	12.9	8.2	2300	1045	510	-	-	-	-	0	0	0	0	0
2953	-	3685	3756	1.9	1.7	3.6	-	-	-	499	-	-	-	0	0	0	0	0
3407	-	3283	3472	5.4	6.9	7.3	-	-	-	-	-	-	-	0	0	0	0	0
3861	3566	3819	3724	10.7	16.0	22.9	1815	-	-	538	-	-	0.07	0.07	0	0	0	0
4315	-	3693	3598	3819	4.2	5.9	-	-	-	510	-	-	0.07	0.07	0	0	0	0
4770	-	-	-	-	-	-	-	-	-	-	-	-	0.14	0.07	0	0	0	0
5224	3377	3377	3377	3377	2525	3.2	1554	-	-	-	-	475	-	-	-	-	-	-
5678	-	3377	3377	3377	3387	14.3	-	-	-	-	-	463	-	-	-	-	-	-
6132	-	3377	3377	3377	3377	2765	2765	-	-	-	-	-	0.14	0.14	0	0	0	0
6587	3914	3914	3914	3914	3914	3787	1649	-	-	-	-	-	0.21	0.21	0.07	0.07	0.07	0
7052	-	3914	3914	3914	3914	3787	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 28. BREAKTHROUGH DATA WITH WESTVACO (STREAM 041A)*

Total Liters	EDC (mg/1) Column						Total Carbon (mg/1) Column					
	Feed	1	2	3	4	5	Feed	1	2	3	4	5
273	-	128	-	-	-	-	-	372	-	-	-	-
636	-	2194	42	-	-	-	-	736	-	-	-	-
999	2398	2241	15	-	-	-	-	-	440	-	-	-
1363	-	-	939	118	-	-	-	-	1600	-	-	-
1726	-	-	-	-	-	-	-	-	-	-	-	-
2090	1768	-	-	1033	-	-	3500	-	-	-	-	-
2553	-	-	-	1957	-	-	-	-	-	-	-	-
2816	-	-	-	-	-	-	-	-	-	-	-	-
3180	-	-	-	1736	-	-	-	-	-	-	-	-

*Flow: 0.76 1/min

Loading: 0.36 1/min-m^2

TABLE 29. BREAKTHROUGH DATA WITH WVG (STREAM 041A)*

Total Liters	Feed	EDC (mg/l) Column				
		1	2	3	4	5
363	2557	-	-	-	-	-
818	-	35	30	-	-	8
127	-	87	-	-	-	16
1726	2730	-	63	-	24	2
2180	-	-	46	-	-	32
2635	-	-	B.T.	17	-	40
3089	2983	-	-	B.T. 260	98	48
	-	-	-	-	33	-

*Flow: 0.95 l/m

Loading: 4.80 l/min-m^2

TABLE 30. BREAKTHROUGH DATA WITH WVG (STREAM 041A)*

Total Liters	Feed	EDC (mg/l) Column				
		1	2	3	4	5
454	-	0	0	0	0	0
908	-	2	-	-	0	0
1362	-	962	0	0	0	0
1817	2919	-	14	0	0	0
2271	-	-	1578	36.5	0	0
2726	-	-	2815	39	0	0
3180	2768	-	2615	2615	24	0
3634	-	-	-	-	694	37
4111	-	-	-	-	-	53
	3440	-	-	-	-	300

*Flow: 0.95 l/min

Loading: 4.81 l/min-m^2

capacities for EDC than the WVG. These findings were contrary to lab studies which showed that WVG was the best for both TC and EDC. To reconcile this discrepancy, one column was repacked with fresh Filtrasorb 400 and a run was made to determine the adsorption capacity. The data shown in Table 26 indicated that the Filtrasorb 400 did have a smaller adsorption capacity for EDC than the WVG. The capacity variance could be explained by lot-to-lot variation from a single commercial source.

The other two runs were to determine the adsorption capacity of the Monochem activated carbon (AC). Laboratory studies had shown that its EDC adsorption capacity was about one-half that of the best commercial AC. Since there was less than 25 kg of the Monochem activated soot carbon, only one column was packed. Unfortunately, the column plugged shortly after start-up. Copious quantities of carbon fines were found blocking the effluent line. Two hours of backflushing solved the problem, and the run was restarted. The breakthrough occurred after 23.5 hr. It was found that the Monochem carbon had an adsorption capacity of approximately 0.16 kg EDC/kg carbon (Table 31). This capacity confirmed earlier laboratory studies since the value was around one-half of the capacity of WVG (0.28 kg EDC/kg carbon).

To determine the effectiveness of steam regeneration on the Monochem carbon, the column was regenerated for 48 hr with 43.3°C steam (0.2-0.34 atm). These two runs confirm earlier findings on the adsorption capacity of the Monochem carbon and indicate that it could be steam regenerated just as readily as the commercial activated carbons.

PROCESS EFFLUENT 081D AND 081A

Introduction

After completing the activated carbon adsorption field tests on stream 041A, it was decided to study a process effluent whose contaminants were more highly chlorinated and whose boiling points were much higher than that of ethylene dichloride. Such organic compounds are tetrachloroethane, perchloroethylene, and trichloroethylene. The higher boiling points of these compounds would make adsorption and subsequent regeneration more difficult than the test work done on stream 041A.

Tests on Process Effluent 081A

The test program was divided into five distinct phases.

1. Breakthrough data for WVG carbon. This commercial carbon had exhibited the overall best adsorptive characteristics for comparative stream service.
2. Furnace regeneration adsorption.
3. Preliminary *in situ* stream regeneration.

TABLE 31. SUMMARY OF CARBON ADSORPTION FIELD TRIALS ON STREAM 041A

Run No.	Carbon Type	Flow Rate (l/min)	Total Run Time (hrs.)	No. of Columns	Carbon Bed			Average EDC Concentration		EDC Retained in Bed (kg)	Carbon Adsorption Capacity	
					Height (m)	Weight (kg)	Volume (m^3)	Influent (mg/l)	Effluent (mg/l)		(kg EDC) / (m^3 Carbon)	(kg EDC) / (kg Carbon)
17*	Monochem	0.84	23.5	1	1.40	10.2	0.025	2468	1115	1.59	65.35	0.16
18	Monochem	0.84	19.5	1	1.40	10.2	0.025	3100	974	2.09	85.85	0.20
19	Filtrasorb 400	0.8	19	1	1.63	11.9	0.03	1794	37	1.52	53.42	0.13

*Run followed by 48 hours of stream regeneration of carbon (in situ).

TABLE 32. ADSORPTION CAPACITY DATA FROM BREAKTHROUGH STUDY OF STREAM 081A
(Westvaco WVG #1 Activated Carbon)

Hour	Liters	Influent Number of Organics Kilograms		Effluent Number of Organics Kilograms		Kilograms Adsorbed	Percent Adsorbed	Cummulative Number of Organics Adsorbed (Kilograms)	Cummulative Number of Organics Adsorbed / (Kilograms of Carbon)	Kilograms of Organics Through Unit
		3-hour Period	Cummulative Total	3-hour Period	Cummulative Total					
0-3	681	0.299	0.390	0.047	0.047	0.343	88.02	0.343	0.075	0.390
3-6	1363	0.273	0.663	0.006	0.053	0.266	97.67	0.610	0.134	0.663
6-9	2044	0.272	0.934	0.007	0.060	0.266	97.49	0.875	0.194	0.934
9-12	2736	0.065	1.000	0.034	0.094	0.031	47.22	0.905	0.201	1.000
12-15	3407	0.249	1.248	0.047	0.141	0.202	81.20	1.107	0.245	1.249
15-18	4088	0.178	1.426	0.002	0.143	0.176	98.97	1.283	0.287	1.426
18-21	4845	0.140	1.566	0.134	0.277	0.006	4.20	1.289	0.287	1.566
21-24	5451	0.138	1.704	0.190	0.467	0.052	37.50 added	1.237	0.273	1.704
24-27	6132	0.063	1.767	0.109	0.576	0.046	47.82 added	1.191	0.265	1.767
27-30	5814	0.025	1.791	0.128	0.704	0.103	422.22 added	1.088	0.240	1.791
30-33	7495	0.146	1.937	0.123	0.827	0.02	15.52	1.107	0.245	1.937
33-36	8177	0.130	2.067	0.081	0.908	0.045	36.63	1.159	0.256	2.067
36-39	8858	0.087	2.155	0.105	1.013	0.018	20.31 added	1.142	0.254	2.155
39-42	9539	0.095	2.249	0.083	1.096	0.011	11.96	1.153	0.256	2.249
42-45	10,932	0.033	2.282	0.062	1.208	0.029	86.30 added	1.124	0.249	2.282
45-48	10,932	0.032	2.314	0.081	1.239	0.049	154.28 added	1.075	0.238	2.314
48-51	11,537	0.035	2.349	0.349	1.274	0.000	00.00	1.075	0.238	2.349
51-54	12,218	0.090	2.439	0.318	1.305	0.058	64.64	1.134	0.251	2.439
54-57	12,787	0.036	2.476	0.039	1.345	0.002	6.17 added	1.131	0.251	2.476
57-60	13,469	0.19	2.495	0.049	1.393	0.029	154.76 added	1.102	0.245	2.495

4. Expanded adsorption field studies.

5. Split sample analytical comparison.

Breakthrough Data

The data gathered from the breakthrough run on stream 081A are shown in Table 32. The breakthrough curve was determined using a hydraulic loading of 3.89 l/m^2/min with a total volume of 28 liters of WVG carbon in one column, at an upflow rate of 3.8 l/min. This hydraulic loading represented the maximum value to be studied.

The EPA "Process Design Manual for Carbon Adsorption"[2] states that in the range of 0.7-3.5 l/m^2 min, the hydraulic loading *per se* seems to have little effect on adsorption capacity. Table 32 indicates an observed adsorption capacity of approximately 0.12 kg organics/kg activated carbon. This value was much less than the 0.30 value observed for this same carbon for streams 221A and 041A. Since the hydraulic loading value was very high, it is possible that the maximum loading was exceeded, thus affecting the adsorption capacity. It is also possible that streams containing more highly chlorinated C-2 hydrocarbons with higher boiling points behave differently than those containing mainly EDC.

Shirco Furnace Regeneration

After saturation by stream 081D, the activated carbon (WVG) was removed and transported in drums to the site of the Shirco furnace for regeneration. The regeneration temperatures and organics removal are shown in Table 33. It would appear that over 95 percent of the organics were removed at listed process conditions.

TABLE 33. REGENERATION OF WESTVACO WVG #1 ACTIVATED CARBON

Stream	081D
Prior No. of Regenerations	0
Mat Condition	Wet
Residence Time (min)	3
Output (kg/hr)	181
Furnace temperature, lamp section	1300-1500
kg organics/kg activated carbon	
Saturated condition	--
Prior to Regeneration	0.0352
Final	0.0009
Furnace Blanket Gas	Nitrogen

Preliminary In Situ Steam Regeneration

Initial tests utilizing 0.20 to 0.34 atm steam required over 60 hr to reduce the TOC and TOD levels in the condensate below 5 mg/l. This long generation time was attributable to the presence of tetrachloroethane, which boiled at 148.9°C, while the regeneration steam temperature was only 110°C. To accomplish this regeneration, sufficient steam would have to be present to lower the partial pressure of the tetrachloroethane sufficiently to cause boiling.

Expanded Adsorption Field Studies

As demonstrated earlier, lower adsorption capacities and longer steam regeneration times were found for activated carbon saturated by the chloroorganics in stream 081A. To study the effect of higher temperature steam regeneration, two Teflon-lined steel columns were installed for further test work on stream 081A.

Table 34 shows a summary of all successful adsorption runs and indicates the total organics present in the influent, effluent, as well as the kilograms of organics adsorbed per kilogram of carbon. The average adsorption capacity of WVG carbon for organics in stream 081A was 0.15 kg/kg carbon. This was approximately one-half the value found for this carbon on streams 221A and 041A.

EDC was the main impurity in streams 041A and 221A. Stream 041A exhibited no chloro-organic heavier than EDC. Stream 221A showed heavier chlorohydrocarbons present in trace concentrations. Stream 081A exhibited chlorohydrocarbons impurities much heavier in greater concentrations than those in stream 041A.

Table 34 shows the average concentration of each component in the influent versus the average percent adsorption for each run. In the previous field tests involving adsorption, there was little marked contrast in the adsorptivity of each component. The data in Table 35 indicate the perchloroethylene is most strongly adsorbed, followed by trichloroethylene, tetrachloroethane, and ethylene dichloride.

The adsorption capacity of WVG carbon apparently was greatly affected by the presence of the larger molecules of perchloroethylene, trichloroethylene, and tetrachloroethane. These three chlorinated hydrocarbons also had a much higher boiling point. All three compounds were present in sufficient quantities to prevent EDC from dominating the adsorption process.

Since the new columns were constructed of Teflon-lined steel, it was possible to regenerate them with an in-plant live steam (Table 36). The steam for regeneration was saturated at 120.1°C, a temperature which has been sufficient to regenerate the carbon completely in streams 041A and 221A.

The data indicate that the steam temperature for stream 081A will have to be higher for complete regeneration. For example, the presence of tetrachloroethane with a boiling point of 145°C indicates the necessity of higher steam temperatures for regeneration, particularly when removal times are shortened to minimize recycling time and equipment usage.

TABLE 34. COMPARISON OF ALL SUCCESSFUL RUNS FOR THE CARBON ADSORPTION UNIT AT SATURATION: STREAM 081D

Run	Carbon Characteristics	Average Influent Conc. (mg/l)	Average Effluent Conc. (mg/l)	Saturation Time	Kilograms Adsorbed	kg Adsorbed / kg of Carbon	Percent Adsorbed
1A	21.9 kg - New	349	36	18 hrs.	1.2	0.12	90
1	15.5 kg - New	180	52	43	1.2	0.17	71
*2	15.5 kg - Reg. 1	148	26	26	0.7	0.095	82
3	15.5 kg - Reg. 2	89	27	33	0.44	0.062	70
4	11.3 kg - New	101	35	54	0.8	0.15	66
5	11.3 kg - Reg. 1	100	31	39	0.57	0.11	69

*Adsorption and Steam Regeneration Data Do Not Agree.

TABLE 35. ADSORPTION DATA ON THE INDIVIDUAL COMPONENTS FOR THE CARBON ADSORPTION UNIT: STREAM 081D

	Kg of Component Through Column / Kg of Total Organic Through Column				Kg of Component Adsorbed / Kg of Component Through Column			
Run	TETRA	PERC	TRI	EDC	TETRA	PERC	TRI	EDC
1A	0.52	0.02	0.03	0.34	0.88	0.98	0.98	0.91
1	0.61	0.11	0.09	0.13	0.81	0.98	0.78	0.10
2	0.73	0.05	0.15	0.05	0.85	0.96	0.93	-0.05
3	0.73	0.12	0.09	0.04	0.70	0.96	0.77	-0.32
4	0.54	0.12	0.15	0.11	0.74	0.96	0.79	-0.11
5	0.68	0.08	0.17	0.05	0.65	0.99	0.76	0.50

The use of steam stripping as a means of regenerating the fixed activated carbon beds has significant technical importance. The exit vapors could be condensed and the organic phase separated and recycled to the process. The aqueous phase could be recycled to the plant effluent. Thus a closed-loop effluent treatment process could be effected, with by-product credit to reduce equipment expenses.

ECONOMIC DISCUSSION

Field trials of the adsorption demonstration units were not very promising. Overall results on stream 041A indicated that, down to a level of 25 mg/l in the treated effluent, approximately 1 kg of activated carbon was needed to remove 0.1 kg of organics. The spent carbon, however, can be regenerated in place with a low-pressure steam. The exhaust vapors from this regeneration technique can be condensed and recycled to the separation process.

Because of the low adsorption efficiency, the operating cost for the adsorption system would be \$3.50 to \$4.50 per kilogram of organics removed. For average inlet concentrations of 2000 mg/l EDC and a nominal flow of 380 l/min from a 32-million kg/yr ethylene dichloride plant, this cost would amount to 4.5 to 7 cents per kilogram of product.

TABLE 36. STEAM REGENERATION DATA FOR THE CARBON ADSORPTION UNIT STREAM 081D

Run	Steam Pressure	Flow Rate (kg/hr)	Regeneration Time[a]	Average Condensate Conc. (mg/liter)	Kilograms Recovered	Percent Recovered
1	30 psig	67	8.2 hr.	599	1.14	94
2	15	42	6.3	-	1.0	157
4	15	41	6.5	455	0.54	70
5	15	40	4.75	-	1.24	178

[a] It was observed that 90 percent of the removable organics were recovered in the first two hours.

SECTION 6

MONOCHEM SOOT CARBON

Soot carbon is generated as a by-product in the manufacture of acetylene via high temperature pyrolysis of air and methane. This material generally accumulates in the process quench water. The soot carbon saturated quench water flows to a settling basin. The carbon floats to the top and is recovered and filtered to a 20 percent carbon and 80 percent water mixture. The consistency of this mixture is that of a fine mud.

Monochem, Inc., which operates an acetylene plant at Geismar, Louisiana, was an active participant in the grant program. By-product soot carbon from this operation approximates 9-million kg/yr. Preliminary indications were that the Monochem soot carbon, if properly prepared, would make a satisfactory activated carbon. In-plant work confirmed that the soot carbon, when predried, did show evidence of activation. However, these evaluations were elementary and not at all conclusive. Therefore, the following program was established to make a definitive evaluation of the adsorption capability of the soot carbon.

1. Preliminary evaluation of Monochem soot carbon for application as a commercial activated carbon.

2. Laboratory and field testing.

3. Developmental program for improving activity and mechanical strength.

4. Laboratory evaluation of binders for better granulation and activation.

5. Compounding, pelletizing, and activating of Monochem soot carbon.

6. Optimization of compounding and activating of Monochem soot carbon.

7. Pilot work on activated carbon density, activation, and regeneration.

8. Isotherm and breakthrough data for Monochem activated soot carbon compared with several commercial carbons.

PRELIMINARY EVALUATION FOR APPLICATION AS A COMMERCIAL ACTIVATED CARBON

The soot carbon discharged from the filter drum had the consistency of a fine mud and a water content of approximately 80 percent. It was necessary to have a final granulated product that could be examined and tested for its adsorptive characteristics. A preliminary experimental program was devised to determine the feasibility of developing a commercially acceptable product. The program included the following steps.

1. Drying of sufficient material to granulate for initial tests and evaluations.
2. Granulating the dried soot into a material suitable for activation and testing.
3. Laboratory scale infrared furnace activation.
4. Laboratory experimental results by iodine number.
5. Laboratory evaluation by isotherm determinations.
6. Laboratory adsorption breakthrough data.
7. Thermogravimetric measurements.

Test samples of granulated soot were obtained by drying the raw material in a commercial steam-heated tube dryer. Stack losses were observed during this process, and may present a problem in commercial practice. Initial granulation was carried out by K-G Industries, Rosemont, Illinois, with a 50-60 CS press using 4.25-11 cm corrugated rolls. Other attempts at pelletizing were made with Simpson Mix Muller, with a ribbon blender, and with a Carver hydraulic bench press.

Batch activation in the laboratory was carried out in metal trays in a furnace that could operate up to 980°C. Preheating to drive off volatiles was investigated at lower temperatures. Steam or other inert gas blankets were furnished to the furnace. The heat transfer was by infrared radiation, leading to an efficient use of power because of the high absorption coefficient of the carbon (black body).

The effects of preheating and activation schedules with two atmospheres during each stage were investigated. The use of a laboratory sized Shirco oven operating on infrared radiation principles offered several advantages in operations.

1. Flexibility of Operation--The preheat and activation temperatures could be obtained quickly because of the application of the heat to the carbon granules.
2. Flexibility of Runs--Since only the carbon is heated, a second run could be made quickly all the way from preheat to activation heat without waiting for the box to cool down.

3. Easy Maintenance--Lamps could be replaced readily. Insulation materials were unaffected by the ups and downs of temperature.

For the preliminary experiments, 50 g of pelletized carbon was placed in the oven. The temperature was recorded by a probe just above the sample. Each experimental trial was evaluated by measurement of iodine number. The results of these analyses, together with the experimental activation conditions are shown in Table 37. Iodine numbers as high as 650 can be obtained from the soot carbon; this compares to values in the range of 80-1,300 measured by the same method for commercial products.

To provide data for isotherms of ethylene dichloride adsorption on the experimentally produced activated carbons, it was necessary to combine batches to obtain adequate sample size. The combinations of trials are listed below:

Blend A: Run # 17, 18, 19, 24, Iodine No. 200 to 300
Blend B: Run # 27, 28, 29, Iodine No. 500 to 600
Blend C: Run # 30, 31, 33, Iodine No. 400 to 500
Blend D: Run # 39, 43, 46, 47, Iodine No. 600 to 700

The adsorption isotherms are shown in Figure 8 for four blends derived from the initial experiments. Blends A and D show high capacity for EDC but only at relatively concentrated aqueous solutions. Blends B and C have a somewhat lower capacity, but operate better at lower equilibrium concentrations.

The EDC adsorptivity of the Monochem carbon was compared with that of three commercial carbons using stream 221A. At a residual EDC concentration of 6000 mg/l, the following adsorptivities were observed:

Monochem (Blend C)	0.75 g EDC/g carbon
Westvaco (WVG - 12 X 40)	1.5 g EDC/g carbon
Calgon (FS - 400)	0.45 g EDC/g carbon
Witco (Witco - 18 x 40)	0.40 g EDC/g carbon

Thus, Monochem Blend C showed better adsorptivity than Calgon (FS-400) or Witco (18 x 40) at 6000 mg/l EDC concentration. However, the commercial carbons showed good adsorptivity over a wider range of EDC residual concentration (10 to 10,000 mg/l) than the Monochem Blend C.

The loss of mass on activation with the schedules shown in Table 37 is a cause of concern. To search for the effect of heat and environment on mass loss, a series of experiments was performed with a Perkin-Elmer thermogravimetric analyzer. Dry powdered soot was subjected to a programmed thermal rise while on the microbalance of the instrument. The atmospheric conditions in the balance compartments were controlled. The results of this analysis are summarized in Table 38.

Equilibrium adsorption experiments indicate the limiting capacity of the carbon as a sorbent. However, in practice, the solution and sorbent do not operate under equilibrium conditions.

TABLE 37. ACTIVATION STUDIES - I

Run No.	Pre-Activation Time	Activation Time	Pre-Activation Gas	Activation Gas	Pre-Activation Temp °C	Activation Temp °C	Iodine Number	Yield Percent
1							< 207	
2							< 177	
3							< 185	
4							< 187	
Darco S-51, as received							511	
5	10	10	Nitrogen	Steam	427	927	410	69
6	15	15	Nitrogen	Steam	427	927	445	55
7	10	10	Nitrogen	Steam	393	927	328	62
8	10	10	Steam	Steam	393	927	416	64
9	15	15	Nitrogen	Steam	371	927	417	63
10	15	15	Nitrogen	Steam	371	927	341	61
11	15	15	Nitrogen	Steam	371	927	429	73
12	15	15	Steam	Steam	371	927	449	71
13	15	15	Steam	Steam	371	927	497	59
14	5	10	Steam	Steam	371	760	< 182	81
15	5	10	Steam	Steam	371	816	< 204	56
16	5	10	Steam	Steam	371	871	242	74
17	5	10	Steam	Steam	371	927	338	76
18	5	10	Nitrogen	Steam	371	760	227	84
19	5	10	Nitrogen	Steam	371	760	266	79
20	5	20	Nitrogen	Steam	371	760	254	79
21	5	10	Nitrogen	Steam	371	871	405	75
22	5	10	Nitrogen	Steam	371	927	517	64
23	0	25		Steam		927	365	73
24	5	20	Nitrogen	Steam	700	816	275	77
25	5	20	Nitrogen	Steam	371	871	372	74
26	5	20	Nitrogen	Steam	371	816	298	77
27	5	20	Nitrogen	Steam	371	927	595	47
28	10	20	Steam	Steam	427	871	569	49
29	10	20	Steam	Steam	427	927	547	49
30	5	20	Steam	Steam	371	871	457	63
31	5	20	Steam	Steam	371	927	484	50
32	5	10	Steam	Steam	482	871	386	73
33	5	10	Steam	Steam	482	927	457	63
34	5-5	5-5	Steam	Steam	427-538	871-888	381	72
35	10	10	Steam	Steam	482-538	943(max)	568	51
36	10	10	Steam	Steam	482-538	871	390	79
37	10	10	Steam	Steam	482-538	871	650	39
38	15	15	Steam	Steam	427	871	541	54
39	15	15	Steam	Steam	427	927	651	40
40	15	15	Steam	Steam	427	871(max)	333	85
41	5+10	15	Steam	Steam	260+427	871	636	61
42	5+10	15	Steam	Steam	260+427	871	581	61
43	15	15	Steam	Steam	427	927+982	659	38
44	15	15	Steam	Steam	427	871	548	59
45	20	15	Steam	Steam	371+538	871	539	63
46	15	15	Steam	Steam	-15 - 93	-9 - 982	664	32
47	10	15	Steam	Steam	538	-8 - 999	648	38
48	5 + 7 1/2 + 7 1/2	15	Steam	Steam	260 + 427 + 538	888	507	61
49	5 + 7 1/2 + 7 1/2	15	Steam	Steam	260 + 427 + 538	893	484	65
50	5 + 7 1/2 + 7 1/2	15	Steam	Steam	260 + 427 + 538	899	563	59
	Witco Chemical Company 18x40 mesh, as received						1264	
	Filtrasorb 400 Calgon Corporation, as received						1248	
	Westvaco Chemical Division 12x40, as received						1314	
	Barneby-Cheney NB-9377						817	
51	15	15	Steam	Steam	538	938	342	68

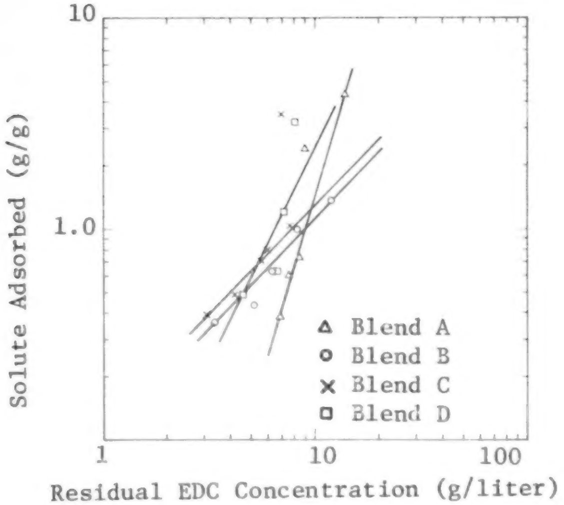

Figure 8. EDC Adsorption isotherm for Monochem activated carbon (stream 221A).

TABLE 38. THERMOGRAVIMETRIC MEASUREMENTS
(Programmed Rate of Heating: 20°C/min)

Medium	Temperature Range °C	Percent Weight Loss NEX[1]	EX[2]
Air	0-800	87.7	27.6
Nitrogen	0-800	27.5	9.9
CO_2	0-700	56.4	18.9

[1] NEX: Not Extracted with Methylene Chloride

[2] EX: Extracted with Methylene Chloride

Through use of breakthrough measurements, mass-transfer parameters were estimated for column design and for performance comparisons of different carbons under dynamic conditions. Four combinations of carbon and wastestream were used in establishing the dynamic behavior expected in the field trials. Two characteristic streams (streams 041A and 221A) were used. The sample of 041A used for these experiments was high in chlorinated hydrocarbons (approximately 8,000 mg/l), was highly alkaline, and showed a total carbon by the Beckman method of approximately 1200 mg/l.

Three carbons were used during the trials: WVG carbon, which previously had shown a high equilibrium adsorption of EDC and total carbon; Filtrasorb-400, which had also shown a high adsorptive capacity; and Monochem activated soot, treated in the laboratory (first activation) to a medium level of activation. The limited amount of Monochem carbon precluded carrying out the complete test program with this carbon.

For each combination, three breakthrough curves were generated at flow rates denoted by L (low), M (medium) and H (high). The range of flow rate was:

L: 0.07 l/min m^2 to 0.14 l/min m^2
M: 0.14 l/min m^2 to 0.25 l/min m^2
H: 0.25 l/min m^2 to 0.35 l/min m^2

Filtrasorb-400 and WVG performed equally in the reduction of EDC for stream 041A (breakthrough curves are included in the Appendix). However, the data indicate that bed life of Monochem sample studies would be only 40 to 50 percent as long as for the two commercial carbons. The Filtrasorb-400 appears to be less sensitive to flow rates than is the WVG in the range studied. The Monochem carbon apparently was not affected by flow rates.

For stream 041A, the minimum TC level obtainable in the carbon column effluent was about 300 mg/l, independent of the type of carbon used. Highest capacity for the solutes in this stream is shown by WVG, followed by Filtrasorb-400, and finally, Monochem. Again, little sensitivity to the flow rates was observed for Monochem. The data indicated that a species other than chlorinated hydrocarbons must contribute to the TC level, and that this species is poorly adsorbed by carbons.

LABORATORY AND FIELD TESTING

Experiments conducted thus far indicated that the soot carbon had potential merit as a commercial activated carbon. The following program was formulated to upgrade the soot carbon to acceptable levels.

1. Drying of sufficient soot carbon for in-depth laboratory and field tests.
2. Granulation of this material by a commercial specialist.
3. Activation in a Herrschoff furnace.
4. Laboratory isotherm and breakthrough measurements.
5. Field tests with activated Monochem soot carbon.
6. Shirco furnace for field activation and regeneration.

Drying, Granulating, and Activating Monochem Soot Carobn

Approximately 1400 kg of the emulsified soot was dried and shipped to K-G Industries for granulation. Due to the fluffiness of the dried material, considerable losses as particulate were noted in the stack of the dryer. This experiment indicated an alternate means of dewatering the raw by-product would be necessary to achieve a granulated product.

The dried soot received by K-G was mixed with 10 percent pitch and granulated by passing the mixed powder through rollers. After sizing, the fines were recycled and the specified material restored in drums. Due to processing losses, only half of the granulated material was recovered. The product exhibited some deficiency in hardness characteristics.

Bartlett-Show, Inc., of California, was contracted to activate the granulated soot in a small Herrschoff furnace over a two-day period. The activation temperature was between 871°C and 927°C. Activation in a multi-hearth furnace revealed (1) the granulated material produced could be activated in this type of furnace and (2) the activated carbon product could be used for development purposes. However, only one drum of activated product was produced from the five drums of feed. A program to generate an additional supply of activated soot carbon was planned after installation of the field activation and regeneration unit.

Laboratory Isotherm and Breakthrough Measurements

Isotherm and breakthrough measurements were carried out for a batch of activated Monochem soot carbon. The granular activated carbon sample was in the form of a very thick slurry in water and contained a considerable amount of carbon fines which were washed off with copious quantities of water. The granules were oven dried at 200°C for approximately 48 hr to ensure complete drying of the carbon. The dried carbon granules were used to make adsorption isotherm and breakthrough measurements. Standard experimental procedures were used for these measurements. The plots are included in the Appendix, and interpretation of these results follows.

Field Tests with Activated Monochem Soot Carbon

As evident from Table 39 at 6000 mg/l EDC, Monochem adsorptivity was 55 percent or less than the adsorptivity of Filtrasorb-400, Witco, and WVG. However, at 1000 mg/l EDC, the adsorptivity of the Monochem carbon was 75 percent or more of the adsorptivity of the commercial activated carbons.

The Monochem activated carbon exhibited a better EDC adsorptivity for stream 221A than for stream 041A. Weber[1] attributes increased organics adsorption to the decreased pH of the water (pH=1 for stream 221A and pH=11 for stream 041A). According to Weber, the increased hydrogen ion concentration neutralizes negative charges at the surface of the carbon, thereby reducing hindrance to diffusion and making available more of the active surface of the carbon. The field trials on stream 041A are summarized in Table 40.

TABLE 39. ADSORPTIVITY OF MONOCHEM AND COMMERCIAL CARBONS
(Stream 221A)

Carbon	Adsorptivity at 6000 mg/1 EDC g EDC/g C	Adsorptivity at 1000 mg/1 g EDC/g C
FILTRASORB-400	0.4	0.15
WITCO	0.45	0.18
WVG	1.5	0.20
MONOCHEM	0.22	0.15

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TABLE 40. SUMMARY OF CARBON ADSORPTION FIELD TRIALS ON STREAM 041A

Run No.	Carbon Type	Flow Rate (liters/min)	Total Run Time (hours)	No. of Columns	Carbon Bed			Average EDC Concentration		EDC Retained in Bed (kg)	Carbon Adsorption Capacity	
					Height (m)	Weight (kg)	Volume (m^3)	Influent (mg/1)	Effluent (mg/1)		$\frac{(\text{kg EDC})}{(\text{m}^3\text{ carbon})}$	$\frac{(\text{kg EDC})}{(\text{kg Carbon})}$
17*	Monochem	0.836	23.5	1	1.39	10.2	0.083	2468	1115	1.6	62.24	0.16
18	Monochem	0.836	19.5	1	1.39	10.2	0.083	3100	974	2.1	81.76	0.20
19	Filtrasorb 400	0.76	19	1	1.63	11.91	0.10	1794	37	1.52	50.88	0.13

*Run followed by 48 hours of steam regeneration of carbon (in situ).

Batch #79 and Batch #104 had adsorptivities of 0.16 g EDC/g carbon and 0.165 g EDC/g carbon, respectively, with stream 221A at 6000 mg/1 EDC concentration. Adsorptivity for Monochem was 0.22 g EDC/g carbon under the identical conditions. Thus, a significant improvement is observed over the two previous activated batches.

The breakthrough profiles indicated a higher rate of adsorption and higher service life for stream 221A than for stream 041A. Two runs were made to determine the adsorption capacity of the Monochem activated carbon on the demonstration unit at process effluent 221A. Lab studies had shown that its EDC adsorption capacity was about one-half that of the best commercially available activated carbon. Since there was less than 25 kg of the Monochem activated carbon, only one column was packed. The breakthrough occurred after 23.5 hrs. The Monochem activated carbon had an adsorption capacity of approximately 0.15 kg of EDC/kg activated carbon (Table 39). This capacity confirms earlier studies, since this value is around one-half the capacity of WVG (0.28 kg of EDC/kg activated carbon).

To determine the effectiveness of steam regeneration on the Monochem activated carbon, the column was regenerated for 48 hrs with 110° steam (0.20-0.34 atm). In the second run, adsorption capacity was slightly increased (0.20 kg EDC/kg activated carbon vs 0.16 kg EDC/kg AC for the first run). These two runs supported earlier findings that the Monochem activated carbon has about one-half of the adsorption capacity of commercial activated carbon and can be steam regenerated just as readily.

Shirco Furnace for Field Activation and Regeneration--

For the field testing program, the soot carbon drying, activation, and regeneration unit had to be large enough to generate sufficient material for the ongoing demonstration unit tests. A recent development in this field was the application of an infrared radiant heat source. Since the furnace size could be regulated by the number of infrared lamps placed in the heating zone, this technology appeared logical for adaptation to this activated soot carbon program. The installation of such a unit offered several other advantages.

1. The furnace could be heated to operating temperature within one hour without damage to the insulation.
2. Air could be restricted so that only the amount required for regeneration was used during the process.
3. There was no mechanical particle breakage within the furance.
4. Simple one-story modular design allowed for easy construction as well as economical expandability.

Shirco, Inc., has applied this technology to the regeneration of activated spent carbon and has been able to approach operating costs of natural gas with an all-electric system utilizing smaller gas scrubber systems, less air, and lower capital investments than other units presently on the market.

The infrared lamps in the system (General Electric) were high-temperature tungsten filament quartz lamps with the filament operating at approximately 2200°C. These lamps radiated 86 percent of input energy, leaving the remaining 14 percent to be dissipated by convection to the cooling air. At rated voltage, the lamps had an average life expectancy of 5000 hrs.

In the carbon regeneration system, the carbon is discharged into the machine onto a conveyor belt. The high temperature belt conveyor carries the carbon through a drying zone and then into an activation zone. In the activation zone, a battery of infrared lamps mounted just above the belt maintains the desired temperature. The belt discharges the carbon into a quench tank at the end of the furnace. The lamps and end seals are cooled by drawing outside air through the cooling air ducts. The temperature is maintained automatically by electronic controllers.

DEVELOPMENT PROGRAM FOR IMPROVING ACTIVITY AND MECHANICAL STRENGTH

Improvements were needed for both the activity and the granulated mechanical strength of the Monochem soot carbon. When measured against a cross-section of commercial carbons, the Monochem soot carbon was shown to have about 50 percent of the adsorption capacity. Further, its crush strength was not very good and limited its regeneration applicability.

Even at a comparative adsorptive value of 50 percent, the activated soot carbon offered some commercial potential. Since it had limited by-product value (heating value over the water content), the only major manufacturing costs were the actual production and depreciation charges. Additional capital equipment would be necessary to accommodate the lower adsorptive capability of the soot carbon. Thus, for a specific commercial application, an assessment would have to be made comparing the lower activated soot carbon cost versus the additional capital equipment costs. However, if a marked improvement could be made in the adsorption capacity and particle strength of the soot carbon, then its competitive position would be greatly improved. Toward this end, a program was initiated to improve the qualities of the soot carbon.

Because of the unanticipated losses in producing the intitial quantity of activated soot carbon for laboratory and field tests, an additional amount had to be dried for granulation and activation. Early in 1974, 450 kg of soot carbon was sent to K-G for granulation. The carbon had been dried in the Shirco furnace under the conditions listed in Table 41. All granulation runs made with carbon dried to the 20 percent moisture level and the 10 percent moisture level using a pitch-binder formulation were unsuccessful.

Several other formulations were tried, and only a 50 percent water/asphalt emulsion gave granules of sufficient hardness to withstand handling. Approximately 10 kg of these granules was returned for activation studies, with a twofold objective: (1) to activate the granules despite the low hardness. (2) to increase the physical hardness, using the activation conditions as a heat treatment.

TABLE 41. SHIRCO DRIED SOOT CARBON

Entering Soot	40-60 Percent Moisture
Exiting Soot	20-25 Percent Moisture
Drying Rate	5.4 - 6.8 kg/hr
Furnace Temperatures	Lamp Section 1 & 2 593-649°C Lamp Section 3 & 4 704-760°C
Blanket Gas	Nitrogen
Total Soot Dried	453.6 kg

The experimental work by K-G Industries to develop a suitable activated carbon from the soot by-product at Monochem covered a period of over one year. In general, efforts were centered around adding binders to previously dried samples of the soot. These binders of conventional character (as pitch) did not produce a granulated material with suitable compaction strengths. Therefore, novel solutions were sought to produce a satisfactory granule.

Physical and Chemical Characterization of Dried Soot

K-G personnel were unable to granulate soot dried on the Shirco furnace, but were able to granulate soot dried in a steam tube furnace. Therefore, experiments were conducted to determine the chemical and/or physical differences between these two soots. One sample each of the steam-tube-dried soot (sample A) and the Shirco dried soot (sample B) was examined by scanning electron microscopy and transmission electron microscopy to determine if any physical differences existed. The differences in granulating behavior, indicated sample A should be radically different in size and degree of aggregation from sample B. However, neither micrograph shows an appreciable difference between the samples in either degree of agglomeration or the ultimate or discrete particle size. Scanning electron micrographs of the carbon black samples as they were dispersed in water and air dried on an aluminum sample holder, and transmission electron micrographs of the samples obtained by drying dilute water dispersions of the carbon black onto collodion membranes are included in the Appendix.

LABORATORY EVALUATION OF BINDERS FOR SOOT CARBON GRANULATION AND ACTIVATION

In this phase of the project, organic and inorganic materials were screened for their ability to bind the soot carbon into a hard, dense form. The adsorbing activity of the processed carbon, as measured by the relative iodine number, was studied.

Previous efforts to determine a suitable binder for Monochem carbon soot concentrated on the use of pitch. The products from various pitch binders were crumbly and had about 50 percent of the absorbing ability of commercial carbons. Development of a suitable activated carbon from the Monochem soot was divided into several research categories.

1. Moisture content of soot carbon and selection of binders.

2. Activation of carbon samples.
3. Measurement of adsorption activity.
4. Further soot carbon development.

Moisture Content of Soot Carbon and Selection of Binders

Initially, work was done with the soot carbon at three levels of water content: (a) soot carbon dried to a water content of 10% (powder dry), (b) soot carbon dried to a water content of 57% (still had caking tendencies), and (c) soot carbon, as received, with a water content of 79% (mud-like in appearance). Each of these samples was evaluated by the addition of different potential binders. The selection of binders is shown in Table 42.

TABLE 42. MATERIAL SELECTION FOR BINDER STUDIES

Test	Conditions of Soot Carbon	Additives as Binder
(a)	Dried to 10% moisture content	Plaster of Paris, Bakelite resin, phenol formaldehyde resins, arofene
(b)	Dried to 57% moisture content	Bakelite, Reichhold 29-353, methocels, starch, bagasse, polyvinyl alcohol, filter cell, cement, calcium carbonate, phosphoric acid, calcium hydroxy phosphate, dental investment, silicone-latex, sodium aluminum oxide.
(c)	As received, 79% moisture content	Methocels and bagasse

The material with 10 percent moisture content was mixed with varying concentrations of the various binders. The mixture was then pressed in a Buehler hydraulic press. During the heating process, the compression die was surrounded by a heating mantle which maintained a temperature of 71-82°C. The material with a moisture content of 51 percent was too wet to use in the hydraulic press but could be extruded in a simple hand-operated unit. Extrusion was chosen as the method of handling the material with 79% moisture content; however, the strands formed a puddle-like mass after being extruded. To eliminate the puddling effect, the carbon was mixed with the binding agent and then dried to about 66 percent moisture. This procedure produced a stable extruded material.

Activation of Carbon Samples

All pressed or extruded samples were subjected to activation by heating in the presence of nitrogen gas. The heating was conducted in a cylindrical furnace manufactured by Aten, Ltd. The furnace had a maximum temperature of 1204°C and was accurate within ±6.7°C. Power was supplied to each half section of the furnace unit by a 10 amp, 140 V rheostat purchased from the W.H. Curtin Company. For all activation heating, the furnace was flushed with dry nitrogen. The entire furnace was wrapped in a ceramic insulation blanket, and additional layers of the blanket were used to protect the counter top.

The activation times and temperatures were chosen on the basis of the previous pitch binder study. The highest activity for the pitch binder was produced by a pre-heating at about 454°C for 15 min, followed by an activation heating at 982°F for 15 min. These same heating conditions were chosen for the present work. However, steam was used to flush the furnace during the heating of the pitch samples in the current study. The use of nitrogen as the inert medium for laboratory evaluation appeared to be as effective as steam, although the water content of the carbon could have been a factor in the activation process.

Laboratory Evaluation of Binders for Granulation and Activation

The evaluation of different binders and their effect on the activity of the Monochem soot carbon was divided into several phases.

1. Pressed pellet study.
2. Extrusion of semi-dry carbon.
3. Extrusion of wet carbon.
4. Further soot carbon development.

Pressed Pellet Study--

The experimental data from the hard pellet samples are summarized in Table 43. For all samples the pressure applied to the press was about 544 atm. The percent of binder in the sample is the percent by weight of the carbon in the sample. The water is tabulated as percent of total weight of the sample. The description of the samples was based solely on a qualitative judgment. Those samples described as hard required a strong pressure to break into two pieces. Those samples listed as brittle were relatively easy to break apart. The designation of homogeneous or nonhomogeneous refers to the distribution of resin within the pellet.

Earlier studies had demonstrated that the 20 percent carbon (80 percent moisture) soot cake coming from the waste soot concentrating process contains an appreciable quantity of extractable organics. Since the drying temperature in the Shirco furnace was approximately 538°C higher than in the steam tube dryer, a greater quantity of organics was expected to be driven off during drying in the Shirco furnace. To test this hypothesis, 1 g each of Shirco dried soot, and 20 percent soot cake was extracted in a Soxhlet extraction apparatus for 24 hrs with 100 ml of chloroform. The chloroform was then distilled off and the residue dried on a steam bath. The results listed below indicate that the Shirco furnace drives off an important binder ingredient. In some way, these extractable organics must aid the dry pitch in penetrating the surface of the discrete particles.

TABLE 43. A TABULATION OF THE DATA FOR THE PRESSED PELLET CARBON SAMPLES

	Composition of Sample		Description of Sample	
Code	Binder	%H_2O	Prior to Activation	After Activation
11	Plaster of Paris-10% mixed dry	10	Very brittle	Hard, nonhomogeneous
12	Plaster of Paris-10% mixed as slurry	10	Hard, homogeneous	Hard, nonhomgeneous
13	Plaster of Paris-10%	51	Sample squeezed out of press	Hard, stratified
P1	Phenol Formaldehyde Reichhold 29-353-15%	10	Hard	Brittle
P2	Phenol Formaldehyde Reichhold 29-389-15%	10	Poor distribution of resin	Brittle
P3	Reichhold 29-389-10%	51	Brittle, very moist	Hard
P4	Reichhold 29-353-12%	51	Very soft	Brittle
P5	Phenol Formaldehyde Arofene-10%	10	Nonhomgeneous	Hard
P6	Arofene-10%	51	Very soft	Brittle
C1	Bakelite-10%	10	Hard	Hard
C2	Bakelite-5%	10	Hard	Hard
C3	Bakelite-2%	10	Hard	Brittle
C4	Bakelite-10%	51	Homogeneous, not as hard as dry carbon	Brittle

Soot Sample	Percent Extractables
20 Percent Cake	10.2
Steam-Tube-Dried	8.5
Shirco-Dried	4.98

Since the steam tube dryer was no longer available to test these findings, 4.5 kg of soot was dried under the soot-burning furnaces to less than 30 percent moisture. The temperature at this location was 66-71°C and would not drive off an appreciable quantity of organics. This soot was shipped to K-G for granulating.

The pressed pellets all were firmly compacted. However, it was believed that this compacting would produce a nonporous carbon structure which would be poorly adsorbent. Therefore, the pellet press method of compacting was abandoned in favor of an extrusion method. The pellet samples were not examined for their ability to adsorb iodine.

Extrusion of Semi-Dry Carbon--

The moisture content of the semi-dry carbon was initially 51 percent. It was found that this carbon was too dry to extrude well. Varying amounts of water were added to the sample to produce a mix which would give smooth, uniform strands and leave only a small amount of material in the grinder. The results from the extruded carbon samples are listed in Table 44. The binders are tabulated as percent by weight of carbon in the sample.

The iodine number was measured for those samples which were judged to be hard or moderately hard. Considering only the iodine number, the sample containing 4 percent methocel HB (hydroxy butyl methyl cellulose) would be the best product. However, the carbon samples containing 8 percent methocel HB showed a greater degree of hardness. The water content of the sample was important when using methocel HB as a binder. For the 8 percent methocel level, the integrity of the extruded strand changes from a compact, smooth strand to a fluted strand as the water content varies.

Two other grades of methocel tested (methocel HG and methocel HC) did not bind the carbon as well as methocel HB. This was probably due to the difference in viscosity among the various grades. Methocel HB has a viscosity of 12,000 cps, whereas methocel HG and methocel HC both have viscosities of 4000 cps.

The samples containing bagasse showed relatively good activity with moderate hardness. It appears that both activity and hardness increase as the concentration of bagasse decreases to about 5 percent. This result is encouraging with regard to the use of a substance such as bagasse as a binder.

Extrusion of Wet Carbon--

The moisture content of the carbon was about 79 percent. Trials with two samples indicated that the carbon was too wet to extrude into discrete strands. The remaining samples were prepared by mixing the appropriate binder with the wet carbon and then drying the mix to about 67 percent

TABLE 44. A TABULATION OF THE DATA FOR THE EXTRUDED CARBON SAMPLES PREPARED FROM SEMI-DRY CARBON

Code	Composition of Sample		Description of Sample After Activation	Iodine Number (Commercial=1084)	Relative Iodine Number (Commercial=1.000)
	Binder	% H_2O			
C5	Bakelite-10%	51	Powder	--	--
C5	Phenol Formaldehyde Reichhold 29-353	Unknown	Soft	--	--
C7	Reichhold 29-353-27%	51	Brittle	--	--
C8	Cement-8%	68.9	Moderately hard	384.05	0.354
14	$CaCO_3$-340%	35.3	Powder	--	--
15	$CaCO_3$-81%	57	Soft, easily broken	--	--
16	Phosphoric Acid-81%	42.6	Soft, easily broken	--	--
17	Calcium hydroxy phosphate-81%	57	Moderately hard	--	--
18	Dental investment-81%	53	Soft	--	--
19	Silcone-latex binder-40 ml of liquid	31	Hard	353.85	0.326
I10	$NaAl\ O_2$-21%	49	Powder	--	--
M1	Methocel HB-8% Phenol Formaldehyde-8%	67	Soft	--	--
M2	Methocel HB-8%	68.9	Hard	570.93	0.527
M3	Phenol Formaldehyde Reichhold 20-353-8%	69	Brittle	--	--
M5(B1)	Bagasse-16.3%	67	Soft	421.57	0.389
M6	Polyvinyl Alcohol-8%	69	Moderately hard	377.10	0.348
M7	Filter Cel-Diatomaceous Earth-8%	69	Brittle	--	--
M8	Starch-8%+0.05M $ZnCl_2$	69	Moderately hard	468.26	0.432
M9	Starch-8%+0.10M $ZnCl_2$	69	Soft	--	--
M10	Methocel HG-8%	69	Soft	--	--
M11	Methocel HC-8%	69	Hard	492.52	0.455
B2	Bagasse-38%	73.6	Very soft	381.98	0.352
B3	Bagasse-8%	69	Moderately hard	465.11	0.429
B4	Bagasse-4.8%	69	Moderately hard	531.16	0.490
B5	Bagasse-8%+0.05M $ZnCl_2$	69	Moderately hard	446.89	0.412
01	Methocel HB-13.6%	69	Moderately hard	--	--
02	Methocel HB-8%	70	Moderately hard	--	--
03	Methocel HB-8.8%	69	Moderately hard	--	--
04	Methocel HB-4%	69	Moderately hard	635.17	0.586
05	Methocel HB-5.7%	69	Moderately hard	500.03	0.488
06	Methocel HB-8%	67	Relatively hard	--	--
07	Methocel HB-8%	68	Hard	389.00	0.379

moisture content. The results from this phase of the work are given in Table 45.

Samples A1 and A2 were each collected as an amorphous mass which was dried and activated. The hardness was determined after activation. Note that the activity of sample A2 is greater than that of A1, indicating that bagasse can increase the adsorbing activity of the carbon. Sample A5, containing 4.7 percent methocel HB and 4.7 percent bagasse, showed the highest activity of all the samples tested. These samples again indicate that the adsorbing ability of the carbon decreases as the weight percent of binder increases. The water content of the sample is very important to the extrudability. The best mix appears to have a moisture content of about 68 percent.

Further Soot Carbon Development

Work to this point consisted primarily of using a wide variety of organic and inorganic compounds as binders for the soot carbon. The moisture content of the carbon and the method of compacting the carbon were varied. All samples prepared during the previous phases of the project were activated in a nitrogen atmosphere. The results of this effort indicated that wet carbon of 73 to 79 percent moisture content can be converted to a hard form by extruding the carbon mixed with 8 percent methocel HB. The activity of this carbon after activation was about 60 percent that of commercial carbon. The price of methocel HB as of January 12, 1976 was quoted as $1.80/kg based on a minimum order of 30,000 kg. At this price, the cost of the binder for one kg of activated carbon containing 8 percent methocel HB would be 14.4¢.

The next objective was to prepare samples using various gum binders and to determine the optimum temperature conditions for activation of the samples. In addition, a brief study of the effect of inorganic additives was conducted. Xanthan gum, guar gum, gum arabic, and various other types of methocel were evaluated; only the methocel was found cost effective.

After completing the examination of natural gum binders, the use of methocel as a binder was reexamined. Methocel HG (hydroxy propyl methyl cellulose, viscosity = 4000 cps) and methocel HC (methyl cellulose, viscosity = 4000 cps) were tested. Methocel HG was found to produce a soft material whereas methocel HC produced a hard product. The difference in the performance of these two binders was believed to result from a difference in chemical composition and solution viscosity. It was decided to investigate a higher viscosity grade of methocel HG in an attempt to produce a hard product.

Samples of methocel J12, methocel K15, and methocel J20 were supplied by Dow Chemical Company. The viscosities of a 2 percent solution of these materials were 12,000 cps, 15,000 cps, and 20,000 cps, respectively. The soot carbon of 73 percent moisture content was processed with these binders.

The results of this study are listed in Table 46. As expected, the binder of highest viscosity, methocel J20, produced the hardest extruded strands. This type and grade of methocel sells for $1.30/kg with a minimum

TABLE 45. A TABULATION OF THE DATA FOR THE SAMPLES PREPARED FROM WET CARBON

Code	Binder	%H_2O	Description of Sample After Activation	Iodine Number (Commercial=1024)	Relative Iodine Number (Commercial=1.000)
A1	Methocel HB-9.5%	79	Very hard Did not extrude	604.66	0.590
A2	Methocel HB-9.5%	79	Moderately hard Did not extrude	659.54	0.644
A3	Methocel HB-4.7%	66.8	Moderately hard	505.27	0.493
A4	Methocel HB-4.7%	66.8	Moderately hard	589.86	0.576
A5	Methocel HB-4.7% Bagasse-4.7%	68.2	Moderately hard	626.32	0.611

order of 30,000 kg. Considering only the cost of the binder, this is a cost of 10.4¢/kg of activated carbon.

As shown in Table 46, the activity of the activated carbon as measured by the iodine number ranged from 33.5 to 33.7 percent that of commercial carbon. Experiments indicate that these low activities may be significantly improved.

TABLE 46. A DESCRIPTION OF SAMPLES PREPARED FROM DIFFERENT TYPES OF METHOCEL

Code	Type of Methocel*	Percent Binder	Description after Activation	Iodine Number (Commercial=1012)	Relative Iodine Number (Commercial=1.00)
010	J12	8	Brittle	381	0.377
011	K15	8	Relatively Hard	370	0.366
012	J20	8	Hard	339	0.335

*The type of Methocel denotes the viscosity of a 2 percent aqueous solution at 20°C. Type J12 would have a viscosity of 12,000 cps at 20°C whereas K15 would have a viscosity of 15,000 cps.

There has been considerable interest in the potential of bagasse as a binding material. Samples containing 4.8, 8, 38, and over 50 percent bagasse were investigated. A sample containing 70 percent bagasse was prepared from soot carbon of 79 percent water content. The extruded carbon strands were dried at 82°C and then heated in a nitrogen atmosphere at 427°C for 15 min and finally at 982°C. The activated sample was brittle when compressed between the fingers, and its activity was less than 30 percent that of commercial activated carbon. These results indicate that if bagasse is to be used as a binder it must contribute less than 50 percent by weight to the sample.

Effect of Inorganic Additives--

The effects of several inorganic salts on the activity of the carbon were investigated. The Encyclopedia of Chemical Technology[3] states that numerous inorganic compounds increase the activity of activated carbon. Among these compounds are the alkaline earth carbonates, chlorides, sulfates, and phosphates. One alkaline earth element, calcium, is a constituent of coconut shells and bones, from which activated carbon has traditionally been made. The effects of calcium carbonate, sulfate, and phosphate on the activity of the soot carbon containing methocel HB as a binder were examined.

Samples were prepared from soot carbon containing 73 percent water and 8 percent methocel HB as a binder. The extruded strands were activated under nitrogen in two heating stages. The first heating was a 538°C for 15 min and the second was at 1038°C for 15 min. The activity of the resulting carbon was measured via the iodine number. The results from this investigation are shown in Table 47. (All the samples were judged to be hard.)

As shown in Table 47, only a small amount of inorganic material was added to the carbon. The amount of added material was deliberately minimized as the results from previous samples (Table 46) indicated that a high concentration of carbonate or phosphate produces a soft product. The presence of either $CaCO_3$ for $CaSO_4$ appeared to decrease the measured activity of the carbon. The activity of the carbon containing $Ca_3(PO_4)_2$ did not seem to be very different from that measured for samples containing only methocel HB.

TABLE 47. EFFECT OF INORGANIC ADDITIVES ON THE ACTIVITY OF SAMPLES METHOCEL HB BINDER

Code	Inorganic Additive	Percent Additive	Description after Activation	Iodine Number (Commercial=1012)	Relative Iodine Number (Commercial=1.00)
M12	$CaCO_3$	0.5	Hard	<296	<0.292
M13	$CaSO_4$	0.5	Hard	<289	0.286
M14	$Ca_3(PO_4)_2$	0.5	Hard	370	0.365

The results from this phase of the project indicate that neither $CaCO_3$ nor $CaSO_4$ is a likely candidate for increasing the native activity of the soot carbon. In higher concentrations, $Ca_3(PO_4)_2$ may be useful in increasing adsorption by the carbon. However, this material is not readily available commercially.

COMPOUNDING, PELLETIZING, AND ACTIVATING MONOCHEM SOOT CARBON

The first step in the optimization of the activation process was to determine the reproducibility of any given activation process. For this procedure, sample K7, containing 1.8 percent Kelzan and 5.5 percent methocel HB, was divided into two portions. Each portion was subjected to essentially the same activation conditions. The measured iodine number of the first portion was 483, which corresponded to a relative iodine number of 47.1 percent. The second portion was analyzed to have an iodine number of 500 and a relative iodine number of 48.9 percent. The difference in iodine number between these two portions is 3.4 percent. This error is about that which could be expected from the method of analyzing the carbon. Results of this experiment indicate that any variation in the activity of a uniform batch of carbon must result from the conditions of activation.

The next investigation was to determine if the carbon could be activated in one heating stage rather than two. For this phase of the project, the temperature conditions and the time of heating were varied. The results from this study, listed in Table 48, clearly indicate that a high temperature heating stage is necessary to produce higher activities. A comparison of samples D7 and K11 activated at low temperatures shows that a slight increase in both time and temperature does not produce a corresponding increase in the activity of the carbon.

TABLE 48. A COMPARISON OF THE ACTIVITY FROM LOW TEMPERATURE HEATING WITH THAT FROM TWO-STAGE HEATING

Sample	Binder(s)	Activation Procedure	Iodine Number (Commercial=1024)	Relative Iodine Number (Commercial=1.00)
D7	Methocel HB-8%	Two-Stage Heating: 15 min at 454°C 15 min at 982°C	389	0.379
D7	Methocel HB-8%	Low Temperature Heating 30 min at 677-760°C	200	0.195
K11	Kelzan-2% Bagasse-5%	Two-Stage Heating: 15 min at 441°C 15 min at 954°C	398	0.388
K11	Kelzan-2% Bagasse-5%	Low Temperature Heating: 15 min at 454°C	200	0.195

The next logical step was to determine if the low temperature heating stage could be eliminated. All attempts to heat the carbon at temperatures of 788-954°C without prior low temperature heating resulted in combustion of the carbon. For one such attempt, the carbon was stored under nitrogen before being placed in the furnace at 954°C. It was hoped that the nitrogen would diffuse into the carbon and displace any free oxygen present. This procedure, however, did not prevent combustion. The two experiments indicated that a two-stage heating procedure was necessary to achieve optimum activity. The low temperature heating was needed to drive off the volatile organic compounds, and the high temperature heating was needed to produce active sites for adsorption.

Next, a procedure was devised to determine what combination of low and high temperatures would produce the maximum activity. The procedure consisted of activating samples at various combinations of temperatures. The low temperature range extended from 315°C to 538°C, and the high temperature range from 871°C to 1038°C. The temperature combinations are illustrated below. Results of the tests are listed in Table 49.

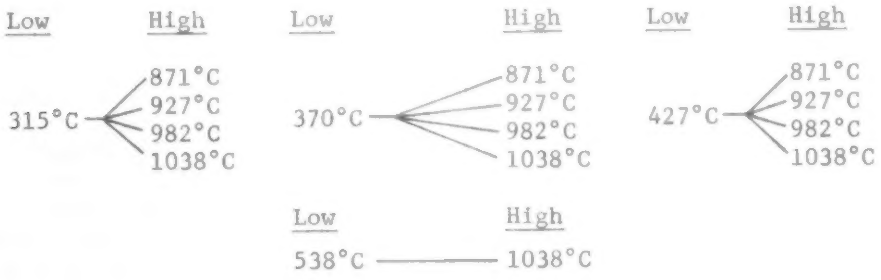

TABLE 49. DETERMINATION OF THE BEST COMBINATION OF LOW AND HIGH TEMPERATURE HEATING CONDITIONS

Activation Temperatures (°C)	Preheat Temperature 315	370	427	538
	Relative Iodine Numbers			
871	0.245	0.265	0.272	
927	0.259	0.280	0.297	
982	0.283	0.325	0.321	
1038	0.312	0.350	0.358	0.370

The carbon used for this procedure was soot carbon of 73 precent moisture content; the binder was 8 percent methocel HB. About 400 g of carbon was used to prepare one large batch of material. All samples were taken from this batch of material to assure uniformity of composition among the samples.

All samples were activated in an inert nitrogen atmosphere. The activation process consisted of heating a sample at one of the low temperatures for 15 min and then at one of the high temperatures for another 15 min. The activation times were held constant for all the samples. The activity of each of the 13 samples was measured in terms of the relative iodine number. The relative iodine number was calculated as:

$$\text{Relative Iodine Number} = \frac{\text{Iodine Number of Test Sample}}{\text{Iodine Number of Commercial Carbon}}$$

The iodine number of the commercial carbon was determined to be 1012.

One sample was pre-activated for 15 min at 260°-343°C and then activated at 954-982°C for 15 min. Another sample was pre-activated at 260-427°C for 15 min and then activated for 15 min at 954-982°C. The samples were stored under nitrogen between the pre-activation and the activation heatings. The samples were quenched in water immediately after the final heating.

The samples activated in steam were compared for relative hardness with those activated in nitrogen. The steam activated samples appeared to be more brittle than those activated under nitrogen. The activity of the steam-activated samples was measured by the iodine number technique. The activity of both steam activated samples was 58 percent that of commercial carbon. A control sample activated in nitrogen atmosphere exhibited only 32 percent of the activity of commercial carbon.

These results indicated that some type of mild oxidizing agent must be present during the activation process to achieve reasonable adsorbing activity. The results also helped explain some of the variation seen in the activity of previous samples.

Determination of Compression Strength--

Compression tests were performed on several strands of the material to quantitate the hardness of the activated carbon prepared from soot carbon with 8 percent methocel HB as a binder. Compression was measured by a Southwark-Emery compression tester. The applied pressure was recorded by a Tate-Emery load indicator. The compression strength was determined for both the lengthwise and crosswise directions. For either direction, the pressure required to break the strand was essentially the same. The maximum applied pressure before crushing the sample was 5 pounds. The diameter in the crosswise direction was 3.175 mm. Using these data, the compression strength of the sample was calculated to be 28.61 Kg/cm^2 (27.7 atm).

Determination of Molasses Number--

The adsorbing ability of activated carbon can be measured in a variety of ways. The iodine number gives an indication of the ability of the carbon to adsorb small molecules. An indication of the ability of an activated carbon to adsorb large, color-producing molecules is given by the molasses number.

A method of determining the molasses number of activated carbon has been described by the Environmental Protection Agency in the Process Design Manual for Carbon Adsorption[2]. The procedure followed in this study was essentially the same as that described by the EPA.

The standard carbon used for this analysis was Calgon Filtrasorb-400. According to a representative of Calgon, the molasses number of this carbon is about 250. The absorbance of this carbon, corrected for the absorbance of the 15 percent sucrose solution blank, was 0.516 absorbance units.

The molasses number was determined for two samples of activated carbon prepared with 8 percent methocel HB as a binder. One sample had been activated in nitrogen and the other sample had been activated in steam. The absorbance of the sample activated under nitrogen, corrected for the sucrose blank, was 0.564, which translates into a molasses number of 228. Although the molasses number for this carbon compares well with that of the commercial carbon, a measurement of the absorbance of the stock molasses solution diluted 1 to 20 revealed that the test carbon had not removed any color producing compounds. The absorbance of the diluted molasses solution was 0.565.

The absorbance of the carbon that had been activated in steam, corrected for the sucrose blank, was 0.469. Using this absorbance, the molasses number was calculated to be 275. This indicates that the steam-activated soot carbon is slightly better than commercial carbon in removing color-producing compounds from molasses.

Large Batch Production--

The furnace assembly previously described had been adequate for the activation of small amounts of material. The production of large amounts of activated carbon required the use of a much larger furnace. On-site in New Orleans was a 15K watt, HG-12 furnace built by Westinghouse which was capable of processing a large amount of material in a short period of time. Repairs and modifications were made to the furnace to make it operational. The furnace had been completely rewired and the standard cell for the pyrometer replaced. The ceiling above the oven was insulated with asbestos and a flue constructed directly above the door of the oven. Tubing was connected to the furnace to provide for either a nitrogen or steam inlet. A stainless steel "basket" 533.4 mm long, 254 mm wide, and 25.4 mm high was constructed to contain the sample during the activation process.

OPTIMIZATION OF COMPOUNDING AND ACTIVATING MONOCHEM SOOT CARBON

Nitrogen versus Steam Activation

Most of the Monochem soot carbon samples prepared to this point had been activated in a nitrogen atmosphere. Based on the iodine number, one sample which was activated in steam was found to have a much higher adsorption activity than a similar sample activated in nitrogen. Several samples were activated both in nitrogen and in steam to determine if the increase in activity was reproducible. Table 50 gives a comparison of the activity of carbon samples prepared from methocel HB and activated in either a steam or a nitrogen atmosphere. The results clearly indicate that activation in steam increases the measured adsorption activity by almost 100 percent over that measured for samples activated in nitrogen.

To further investigate the effect of activation gases on the carbon adsorption capacity, a fresh batch of carbon was prepared and activated in both nitrogen and steam. Two control samples were activated, one in nitrogen and one in steam. Table 51 lists the results derived from this experiment. The results indicate that steam increases the activity when used during the high temperature activation, but does not seem to have much effect during the pre-activation heating. One disturbing result of this study was the sharp decrease in the iodine number for the steam activated sample compared with the steam-activated samples described in Table 50. The only difference between the samples described in Table 50 and those in Table 51 was the lot of methocel HB which was used in carbon preparation.

The next step was to compare the adsorption activity for carbon samples prepared from several different lots of methocel HB. Dow Chemical supplied a new sample of methocel HB. Three different batches of carbon were prepared: one from an old batch of methocel (Lot No. 121693), one from the methocel used for the samples described in Table 52 (Lot No. MM030458B), and one from the new batch of methocel (Lot No. MM030463B).

As shown, the activity of the carbon as measured by the iodine number varied with the particular lot of methocel HB used in sample preparation. It was learned from Dow Chemical that Lot No. MM030458B consisted of methocel HB which had less methyl substitution than the other two lots of methocel. Furthermore, this lot of methocel did not meet product specifications in terms of nonaqueous solution viscosity. However, Dow stated that Lot No. MM030463B was representative of the typical quality of methocel which the firm manufactures.

Finally, the carbon activity was measured by the molasses number procedure. The results from these measurements are given in Table 53. Carbon activated by steam has a greater ability to decolor molasses than does

TABLE 50. COMPARISON OF ACTIVITY FOR METHOCEL HB SAMPLES ACTIVATED IN NITROGEN AND IN STEAM

Activation Gas	Description of Sample After Activation	Iodine Number (Commercial=1012)	Relative Iodine Number (Commercial=1.00)
Nitrogen	Hard	362	0.358
Nitrogen	Hard	322	0.318
Steam	Brittle	588	0.581
Steam	Brittle	584	0.577
Steam	Moderately Hard	471	0.465

Activation of wet strands produced a soft product with a low iodine number: <281, relative iodine number: <0.278.

TABLE 51. ACTIVATION BY TWO DIFFERENT GASES: NITROGEN AND STEAM

Pre-Activation Gas	Activation Gas	Relative Iodine Number (Commercial=1.00)
Nitrogen	Nitrogen	0.257
Steam	Steam	0.322
Nitrogen	Steam	0.388
Steam	Nitrogen	0.218

ACTIVATION CONDITIONS:

Pre-Activation Time (Minutes)	Pre-Activation Temperature (°C)	Activation Time (Minutes)	Activation Temperature (°C)
15	427-454	15	954-999

TABLE 52. ACTIVITY MEASURED FOR DIFFERENT LOTS OF METHOCEL HB

Lot Number	Activation Gas	Iodine Number Commercial=1012	Relative Iodine Number Commercial=1.00
121693	Nitrogen	322	0.318
121693	Steam	588	0.581
MM030458B	Nitrogen	<260	<0.257
MM030458B	Steam	<326	<0.322
MM030463B	Nitrogen	357	0.353
MM030464B	Steam	607	0.624

TABLE 53. ACTIVITY DETERMINATION BY THE MOLASSES NUMBER

Sample	Activating Gas	Absorbance	Molasses Number	Relative Molasses Number	Relative Iodine Number
Calgon	---	0.430	250	1.00	1.00
019	Nitrogen	0.562	191	0.764	0.353
020	Nitrogen	0.547	196	0.784	0.318
020	Steam	0.512	209	0.836	0.465
013	Steam	0.470	228	0.912	0.577

carbon activated by nitrogen. For this series of samples, the activity of the steam activated carbon was almost 100 percent of that measured for the commercial carbon.

Benzene, 1,2-dichloroethane (EDC), phenol, and chloral hydrate were studied by means of Freundlich adsorption isotherms. In addition to these individual compounds, stream 231-A, containing toluene diisocyanate, was investigated. The carbon used for the isotherms was prepared by extruding the Monochem carbon with methocel HB.* One large batch of the carbon was prepared and activated in a nitrogen atmosphere. The relative iodine number for this carbon was 28 percent that of commercial carbon.

The results from the Freundlich isotherms generated from nitrogen activated carbon are given in Table 54. The individual isotherms for each compound are shown in the Appendix. The results for each of the compounds show that the Monochem carbon is better than commercial carbon in the removal of 1,2-dichloroethane, benzene, and acidified phenol. The activated Monochem carbon is not as good as commercial carbon when applied to alkaline phenol, chloral hydrate, or stream 231-A.

The results indicate that, of the compounds studied, only phenol in acid solution could be completely removed from solution by adsorption. When the solution was made basic, a phenol residual of 32 mg/l resulted. The residual in all cases was estimated by extrapolating the adsorption isotherm curve to the x-axis. It is possible that the actual curve would intersect the x-axis at higher residual concentration than those estimated by a straight line extrapolation. If this were so the minimum adsorption limit would be greater than zero.

TABLE 54. RESULTS FROM FREUNDLICH ADSORPTION ISOTHERMS: NITROGEN GAS USED IN ACTIVATION OF CARBON

Compound	pH	C_o (mg/l, TOC)	Ultimate Carbon Loading Factor $\frac{\text{mg TOC}}{\text{gm C}}$ or Residual Compound	
			Monochem	Commercial (Calgon)
1,2-dichloroethane	4.80	159	21 mg/l residual	27 mg/l residual
Benzene	6.55	77.4	10 mg/l residual	14.5 mg/l residual
Phenol	5.93	810	15.31 $\frac{\text{mg TOC}}{\text{gm C}}$	13.18 $\frac{\text{mg TOC}}{\text{gm C}}$
Phenol	11.7	768	32 mg/l residual	4.29 $\frac{\text{mg TOC}}{\text{gm C}}$
Chloral hydrate	6.45	97	35 mg/l residual	6.4 mg/l residual
Stream 231A-TDI	11	630	600 mg/l residual	400 mg/l residual

---

*It was later discovered that the batch of methocel HB which was used did not conform to specifications. This accounts for the low iodine number of the carbon.

Regeneration Studies

In practice, most of the carbon used for wastewater treatment has been regenerated one or more times. The regeneration of activated carbon is usually performed by heating in an oxidizing atmosphere to volatilize adsorbed organic compounds and to create additional micropores. The process results in a change in the adsorption characteristics of the activated carbon. These effects of regeneration on the adsorption capacity of the activated carbon were investigated.

The regeneration study was carried out by collecting the Monochem carbon which was used for the alkaline phenol adsorption isotherm. This carbon was washed with distilled water and dried at 100°C. The carbon was then regenerated by heating at 1000°C for 15 min in a nitrogen atmosphere. Fumes were evolved during the heating process. The commercial carbon (Calgon), which was also used for the alkaline phenol isotherm, was regenerated in the same manner.

The results from the reactivation study are listed in Table 55 and illustrated in Figure 9. The data indicate that these reactivation conditions are not sufficient for complete regeneration of either the Monochem or the commercial carbon. Higher temperatures and an oxidizing atmosphere apparently are necessary for complete regeneration.

The final adsorption isotherms were performed with Monochem carbon which had been activated in steam. Benzene and phenol were studied in this set of experiments. The activated carbon was prepared by preheating in steam at 427°C for 15 min followed by a heating at 982°C for 15 min. The iodine number for this carbon was 41 percent that of commercial activity.

The results from the Freundlich isotherms generated from steam activated carbon are shown in Table 56. The individual isotherms are illustrated in the Appendix. A comparison with the nitrogen activated carbon shows that the steam activated carbon is more efficient in removal of acidic phenol but less effective in removal of benzene.

TABLE 55. RESULTS FOR REACTIVATION OF CARBON AS MEASURED BY PHENOL ADSORPTION

	pH	TOC (ppm)	Ultimate Carbon Loading $\frac{\text{mg TOC}}{\text{g C}}$ or Residual Compound	
			Monochem	Commercial
Virgin Carbon	11.7	768	32 mg/l residual	4.29 $\frac{\text{mg TOC}}{\text{g C}}$
Regenerated Carbon	11.7	902		2.2 mg/l residual

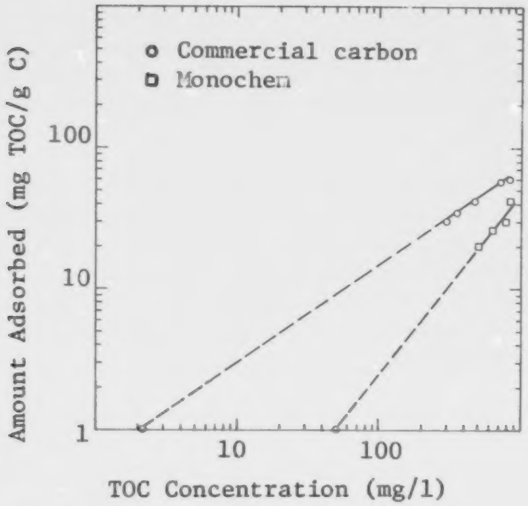

Figure 9. Adsorption isotherm for phenol on regenerated carbon.

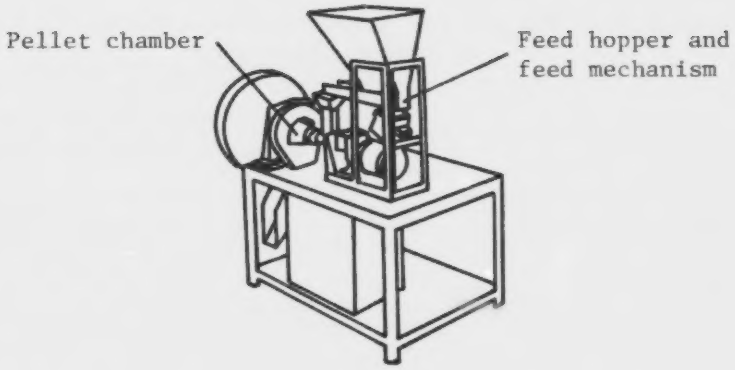
Pellet chamber
Feed hopper and
feed mechanism

Figure 10. Laboratory pellet mill.

TABLE 56. RESULTS FROM FREUNDLICH ADSORPTION ISOTHERMS: STEAM USED IN ACTIVATION OF CARBON

			Ultimate Carbon Loading Factor $\frac{\text{mg TOC}}{\text{g C}}$ or Residual Compound	
Compound	pH	TOC (ppm)	Monochem	Commercial
Benzene	5.5	250	18.5 ppm residual	14.5 ppm residual
Phenol	8.5	1194	24 $\frac{\text{mg TOC}}{\text{g C}}$	13.18 $\frac{\text{mg TOC}}{\text{g C}}$

PILOT WORK ON ACTIVATED CARBON DENSITY, ACTIVATION AND REGENERATION

Up until this point in the program, the laboratory samples of carbon had been prepared from bench equipment. It was decided to perform development work on pilot-scale equipment.

1. Pelletizing for increased density.
2. Small furnace activation procedure.
3. Large furnace.

Pelletizing for Increased Carbon Density--

Extruded samples prepared during these studies were extruded through a household-type meat grinder. This "extruder" had a limited ability to compact the carbon. As a result, the density of the carbon was very low compared with commercial activated carbons. When activated in steam, the hand-extruded carbon became very soft and crumbly.

In an attempt to increase the hardness and the density of the carbon, 45 kg of carbon mixed with methocel HB was shipped to the California Pellet Mill Company for extrusion. An illustration of the pellet mill is shown in Figure 10. The pelletizing operation is described below.

The carbon shipped for extrusion initially contained 64 percent water. When some of this material was run through the pellet mill, it was found to be too moist to give a good compaction. When dried to a moisture content of 53 percent, the carbon mixture extruded well and gave good, compact pellets. The extruded pellets were shipped back to GSRI where they were thoroughly dried.

The apparent density of each of the pelletized samples was measured by filling a weighed 100 ml graduated cylinder with the carbon in a specified time period[2]. The pelletized carbons were activated by heating in steam. The apparent densities of the activated carbons were determined in the same manner used for the unactivated carbon. The apparent densities of the activated and unactivated pelletized carbons were compared with the apparent densities of commercial activated carbons and with carbon extruded by hand through the meat grinder. The results of this comparison are shown in Table 57.

TABLE 57. COMPARISON OF THE APPARENT DENSITY OF VARIOUS CARBONS

Carbon	Moisture Content	Die Size	Apparent Density (kg/m^3)
Westvaco (Nuchor)			682.92
Calgon			452.76
Monochem-Nitrogen Activated	73%	hand-extruded	297.53
Pelletized Monochem-Unactivated	64%	25.4 mm	302.74
Pelletized Monochem-Unactivated	64%	38.1 mm	354.48
Pelletized Monochem-Steam Activated	64%	38.1 mm	350.11
Pelletized Monochem-Unactivated	57%	38.1 mm	381.53
Pelletized Monochem-Unactivated	53%	38.1 mm	396.98
Pelletized Monochem-Steam Activated	53%	38.1 mm	389.76

The pelletizing process produces a marked improvement in the apparent density of the carbon over that achieved by hand-extrusion. The results also indicate that the apparent density of the carbon increases as the moisture content decreases. At a 53 percent moisture content, the apparent density of the carbon approaches that exhibited by the Calgon activated carbon. It should be noted that the high apparent density measured for the Westvaco activated carbon was due to an excessive amount of fines in the carbon sample. The Calgon carbon and the pelletized Monochem carbons contained almost no fines. The results show that steam activation decreases the apparent density only slightly.

The increase in carbon density achieved by use of the California Pellet Mill was encouraging. With the pellet mill, it was possible to: (1) vary both moisture content and binder concentration and (2) process large amounts of carbon and thus achieve uniformity in the final activated carbon.

Optimization of the Steam Activation Procedure Using Small Furnace

The optimzation of the activation procedure using nitrogen as an inert atmosphere had fairly well established its limitations. The results from this optimization indicated that a high preactivation temperature (482°C) and high activation temperature (1038°C) were required to achieve maximum adsorption capacity. The preactivation and activation times were held constant at 15 min each for the entire optimization procedure. The flow rate of nitrogen was not varied.

The use of steam as an activation gas necessitated the repeat of the optimization procedure. Activation by steam required the optimization of the following parameters: activation time, activation temperature, and flow rate of steam. The preactivation heating was held constant at 427°C for 15 min throughout the optimization procedure. It was necessary to carry out two separate optimizations--one for the small cylinder furnace, and one for the large Westinghouse furnace--because the large furnace was not thermostatically controlled above 938°C. The overall procedure consisted of four separate phases:

1. Activation of the carbon under varying conditions.
2. Determination of the percent weight loss due to activation for selected samples.
3. Measurement of the static compression strength of the activated pellets.
4. Measurement of the adsorption capacity by the iodine number method.

All samples were taken from the same batch of carbon which contained 53 percent water and 7.4 percent methocel HB. The carbon-binder mix had been extruded through the California Pellet Mill into uniform pellets about 6 mm long and 3 mm in diameter. Steam was introduced by pumping water through a stainless steel tube directly into the furnace. Since the temperature of the furnace was well above the boiling point of water, steam was produced as the water exited the tube. The amount of steam produced was controlled by regulating the flow rate of water through the Masterflex pump. Two different flow rates, 3.4 and 4.6 ml of H_2O/min, were chosen for study. Above a flow rate of 4.6 ml/min, it was difficult to control the furnace temperature. The volume of the small furnace was measured to be 3800 cm^3. At the lower flow rate, the "water" concentration within the furnace was 5.95×10^{-4} ml/cm^3-min. At the higher flow rate, the concentration was 12.10×10^{-4} ml/cm^3-min.

Samples were activated under the conditions listed in Table 58. The entire set of samples was preactivated at 427°C for 15 min. The percent of weight loss was determined for samples 7, 8, 11, 12, 19, 20, and 23-27. During the heating of sample 28, the steam flow stopped and the carbon burned. The percent of weight loss was determined by weighing the carbon prior to and subsequent to activation. After the preactivation heating and after the activation heating, the samples were stored in a desiccator under dry nitrogen. This prevented a weight change due to uptake of moisture. The results from this study are given in Table 59. With the exception of samples 23 and 24, the results indicated that higher activation temperatures and longer activation times produce a higher weight loss of carbon. No immediate explanation can be given for the discrepancy in the results from samples 23 and 24.

Following the activation procedure, the static compressibility of the samples was measured in a Plexiglas sample holder to quantitate the hardness of the carbon after activation. The pellet was held in place by carefully lowering the Plexiglas cover onto the pellet. A 19.1 mm recession and a smaller indentation in the cover allowed the cover to slide easily onto the base. Calibrated weights were applied directly to the cover to compress the pellet. Weights were added until the pellet crushed.

TABLE 59. RESULTS FROM THE ANALYSIS OF CARBON WEIGHT LOSS DURING ACTIVATION

Sample	Rate of Water Flow (ml/min)	Activation Time (min)	Activation Temp (°C)	Percent of Weight Lost
7	3.4	15	982	42
8	3.4	15	1038	52
11	3.4	20	982	51
12	3.4	20	1038	86
25	3.4	30	982	64
26	3.4	30	1038	85
19	4.6	15	982	62
20	4.6	15	1038	80
23	4.6	20	982	43
24	4.6	20	1038	65
27	4.6	30	982	88
Weight loss due to pre-activation	3.2	15	427	13

TABLE 58. ACTIVATION CONDITIONS FOR OPTIMIZATION OF SMALL FURNACE

Lower Pump Speed: 3.4 ml/min of water flow

Activation Time:	10 min.		15 min.		20 min.		30 min.
Sample	Activation Temperature (°C)	Sample	Activation Temperature (°C)	Sample	Activation Temperature (°C)	Sample	Activation Temperature (°C)
1	871	5	871	9	871		
2	927	6	927	10	927		
3	982	7	982	11	982	25	982
4	1038	8	1038	12	1038	26	1038

Higher Pump Speed: 4.6 ml/min of water flow

Activation Time:	10 min.		15 min.		20 min.		30 min.
Sample	Activation Temperature (°C)	Sample	Activation Temperature (°C)	Sample	Activation Temperature (°C)	Sample	Activation Temperature (°C)
13	871	17	871	21	871		
14	927	18	927	22	927		
15	982	19	982	23	982	27	982
16	1038	20	1038	24	1038	28	1038

Table 60 lists the results accumulated from the compression tests. Most tests were performed in duplicate to account for sample variation. The area was calculated from the cylindrical surface of the pellet.

The results point out several features of the pellets and the activation process. First, there is a wide variance in the crush pressure for several of the samples. This variance does not correlate well with the variance in the external dimensions of the pellets. It is believed that the observed variation is the result of differences in the distribution of pellet activation. Second, the average crush pressure does not seem to be a function of the activation conditions. Only at the longest activation times and highest activation temperatures was there a significant decrease in the average crush pressure. The majority of the samples exhibited a very good crush pressure. These results indicate that a satisfactory sample hardness can be achieved under typical activation conditions.

The adsorption capacity of the activated carbon was determined by the iodine number method. Iodine numbers were also determined for samples of Westvaco and Calgon commercial carbons. The relative iodine number was calculated for each of the activated samples according to the relationship:

$$\text{Relative Iodine Number} = \frac{\text{Monochem Iodine No.}}{\text{Commercial Carbon Iodine No.}} \times 100$$

The calculated relative iodine numbers are given in Table 61.

A remarkable increase in the adsorption capacity of the carbon was achieved through optimization. Capacities were comparable to, and in some cases exceeded, commercial activities. However, there was some concern about reproducibility of the results. To check for reproducibility, the activation procedures for several of the samples were repeated. These results are tabulated in Table 62 and indicate that the high adsorption capacities are reproducible and not artifacts.

The carbon activity data, as measured by the iodine number, correlates well with the results from the weight loss analysis. The highest activities were achieved at the expense of a high weight loss. This is a reasonable result as the activation proceeds by the burn-off of carbon, creating innumerable micropores. If a 50 percent weight loss is considered acceptable, then the optimum conditions are as follows:

Water flow	3.4 ml/min
Activation time	20 minutes
Activation temperature	982°C
Expected percent weight loss	51 percent
Measured range of relative iodine numbers	101 - 114 percent

Optimization of the Steam Activation Procedure Using the Large Furnace

There were two major restrictions on the optimization of the large furnace. First, the maximum temperature was 927°C. Second, the Masterflex pump could not deliver sufficient water to achieve the same steam concentrations as were created in the small furnace. With these two limitations in

TABLE 60. RESULTS FROM THE COMPRESSION TESTS

Sample	Crush Weight (kg)	Crush Pressure (kg/cm^2)	Average Crush Pressure (g/cm^2)	Variance About the Average
1 A	8.62	131	1923	--
	--	--	--	--
2 A	5.06	81	1346	±167
B	6.44	103		
3 A	2.56	46	888	±210
B	4.40	75		
4 A	2.39	41	1020	±413
B	5.57	96		
5 A	3.53	66	847	±122
B	2.53	49		
6 A	5.90	106	1710	±155
B	7.57	127		
7 A	5.42	85	1156	± 98
B	4.34	72		
8 A	7.57	156	1740	±553
B	3.69	81	1740	
9 A	1.51	29	1056	±636
B	6.54	115		
10 A	3.70	68	1205	±201
B	4.34	96		
11 A	3.00	61	1040	±142
B	4.43	80		
12 A	3.04	69	1481	±469
B	6.54	133		
13 A	8.44	141	1828	±238
B	6.93	108		
14 A	9.13	159	2256	± 87
B	8.98	147		
15 A	8.11	142	2317	±225
B	8.98	173		
16 A	3.95	66	1134	±163
B	5.66	88		
17 A	4.42	76	1806	±690
B	7.91	170		
18 A	7.36	128	1868	± 6
B	7.87	127		
19 A	6.50	118	1269	±461
B	3.20	55		
20 A	2.56	53	872	± 88
B	3.86	65		
21 A	2.17	37	995	±449
B	4.72	98		
22 A	4.21	77	1301	±162
B	5.92	99		
23 A	4.30	77	1954	±823
B	10.99	189		
24 A	5.95	104	1025	±497
B	1.39	36		
25 A	5.62	102	1414	± 80.9
B	5.08	91		
26 A	0.91	17	251	
	--	--	--	--
27 A	0.83	17	268	± 23
B	1.03	20		

TABLE 61. RELATIVE IODINE NUMBERS: PERCENT OF COMMERCIAL CARBON (WESTVACO) ACTIVITY*

Activation Time	10 min.	15 min.	20 min.	30 min.
Rate of Water Flow 3.4 ml/min.	1 1600 43%	5 1600 46%	9 1600 56%	
	2 1700 52%	6 1700 66%	10 1700 86%	
	3 1800 67%	7 1800 81%	11 1800 114%	25 1800 100%
	4 1900 73%	8 1900 84%	12 1900 102%	26 1900 130%

Activation Time	10 min.	15 min.	20 min.	30 min.
Rate of Water Flow 4.6 ml/min.	13 1600 47%	17 1600 54%	21 1600 55%	
	14 1700 50%	18 1700 65%	22 1700 64%	
	15 1800 60%	19 1800 75%	23 1800 80%	27 1800 160%
	16 1900 76%	20 1900 105%	24 1900 121%	28 1900 Sampled Burned

*Key to Table 61: Sample Number Activation Temperature
Percent of Commercial Activity

TABLE 62. DETERMINATION OF REPRODUCIBILITY OF ACTIVATION RESULTS

Sample	Activation Time (min)	Activation Temperature (°C)	Relative Iodine Numbers 1st Run	Relative Iodine Numbers 2nd Run
7	15	982	81%	72%
8	15	1038	84%	89%
11	20	982	114%	101%
12	20	1038	102%	136%
19	15	982	75%	103%
20	15	1038	105%	130%
23	20	982	80%	92%
24	20	1038	121%	97%

mind, the activation temperature and the water flow were held constant and only the activation time was varied. The activation temperature was set at 927°C and the Masterflex pump was adjusted to its highest setting at which it delivered 25 ml of water per minute. (To produce the same steam concentration in the large furnace as was produced in the small furnace, the pump would have had to deliver 74 ml of water per min.) The activation times were 15, 30, 45, 60, and 120 min.

Steam was introduced into the large furnace by pumping water through stainless steel tubing which ran first through a small preheater and then into the large furnace. The preheater was heated to 538°C. The water passing through the preheater was vaporized into steam which then entered the large furnace. The samples were activated by heating at 427°C for 15 min and then at 927°C for one of the selected times. The carbon was stored under nitrogen between the preactivation and the activation heating stages. Immediately after activation, the carbon was dumped into water to prevent it from burning.

Samples activated in the large furnace were analyzed to determine the compression strengths and iodine numbers. The samples were analyzed according to the procedures described for the small furnace. The results of these analyses are listed in Table 63 and illustrated in Figure 11. The results show that the compression strength does not vary greatly with the length of activation. In addition, the activity of the carbon is a linear function of activation time up to one hour. Beyond one hour, the linear relationship ceases; however, the activity of the carbon continues to increase even after two hours of activation. It was deemed impractical to continue activation times beyond 2 hrs, so the activation time was chosen to be 2 hrs. This concluded the optimization procedure.

COMPARATIVE ISOTHERM AND BREAKTHROUGH DATA

It is important to generate isotherm and breakthrough data in direct application to a wastewater under investigation. Data gathered under laboratory conditions with pure water may not be relevant to a particular process effluent. Therefore, for final evaluation, a set of experiments was developed using isotherm and breakthrough data for several of the process streams studied in this program. The experiments compared the best developed activated Monochem soot carbon with several commercial carbons. Three facets of this study were:

1. Isotherm determinations and comparisons.

2. Breakthrough data for the Monochem active soot carbon compared to the best commercial carbon from the isotherm data.

3. Regeneration of readsorption evaluation of Monochem active carbon and Nuchar carbon.

Four activated carbons were used for each of the above tests: Calgon-400, Nuchar WVC, Barneby-Cheney, and Monochem activated soot carbon optimum. The Monochem activated soot carbon represented a recipe with methocel HB

TABLE 63. RESULTS FROM COMPRESSION TESTS AND IODINE NUMBERS: SAMPLES ACTIVATED IN LARGE FURNACE

Sample	Activation Time (min)	Average Crush Pressure (kg/cm^2)	Relative Iodine Number (commercial-100%)
1	15	117	44%
2	30	95	52%
3	45	95	65%
4	60	56	71%
5	120	--	84%

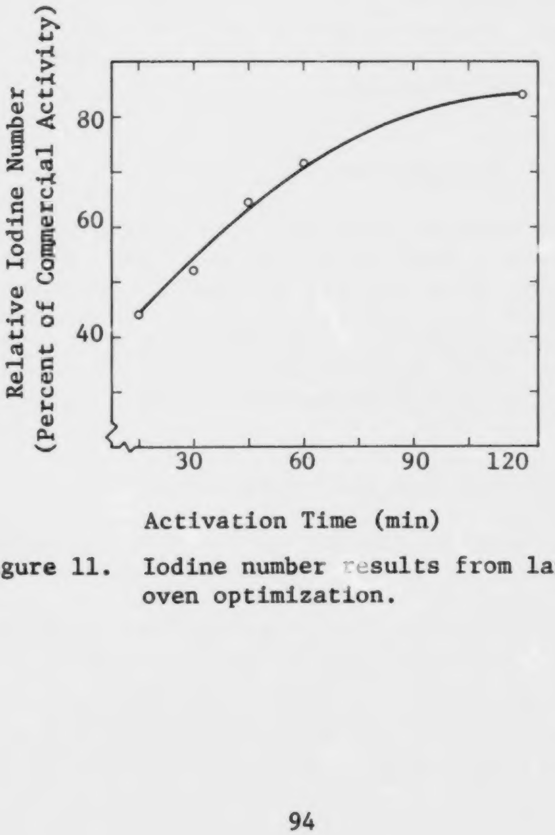

Figure 11. Iodine number results from large oven optimization.

which had been preactivated for 15 min at 437°C and activated at 927°C in the presence of steam. The best of the three commercial carbons was selected from these isotherm tests to make continuous flow determinations comparison tests with the Monochem carbon.

Three process effluents were selected for isotherm determinations. In addition to the tests on raw effluents, the effects of various treatment sequences on the ability of activated carbon to remove trace contaminants were determined. Consequently, the following tests were planned:

Isotherm Determinations--

Stream 231-A--No pretreatment raw process effluent; ozonated process effluent; biotreated; ozonated followed by biotreatment; pretreatment by acidification and filtration; pretreatment by acidification and filtration followed by biotreatment.

Stream 221-A--After steam stripping; after steam stripping and ozonation.

Stream 351-A--No pretreatment.

Breakthrough Data--

Stream 231-A--No pretreatment raw process effluent; ozonated process effluent; biotreated; ozonated followed by biotreatment; pretreatment by acidification and filtration; pretreatment by acidification and filtration followed by biotreatment.

Stream 221-A--After steam stripping; after steam stripping and ozonation.

Stream 351-A--No pretreatment.

Regeneration--

Stream 231-A--No pretreatment raw process effluent; ozonated process effluent; biotreated; ozonated followed by biotreatment; pretreatment by acidification and filtration; pretreatment by acidification and filtration followed by biotreatment.

Stream 221-A--After steam stripping; after steam stripping and ozonation.

Stream 351-A--No pretreatment.

Isotherm Determinations and Comparisons

All three commercial activated carbons were readily available. The Monochem carbon was preactivated for 15 min at 427°C and activated for 2 hrs at 927°C, utilizing steam as the activation medium. Tabulation of the influent and residual conditions for the various experiments are given in Table 64. Plots of the isotherm data are given in the Appendix. The isotherms show that Monochem continues to adsorb better than the Calgon carbon; however, Barneby-Cheney adsorbs better than Calgon on some treated streams, and Nuchar adsorbs better than Calgon on other streams. By comparing the residual concentration and/or ultimate loading factor, Nuchar seemed to be the best of the three commercial activated carbons.

TABLE 64. TABULATION OF MULTICOMPONENT ISOTHERM RESULTS
(Steam Activation Gas)

				Residual Concentration mg/1 TOC				Ultimate Carbon Loading Factor mg/TOC/MC	
Stream	Treatment	pH	Influent TOC(mg/1)	Monochem	Calgon	Nuchar	B-C	Nuchar	B-C
231A	Raw	12.0	235	17	34				
231A		12.3	419					0.89	1.64
231A	Acidified	2.5	224	35	40				
231A		7.0	333					1.3	1.0
231A	Ozonated	11.8	147	Nonequilibrium					
231A		>11	193						
231A	Biotreated	8.3	144	23	29				
231A		8.9	143			20	52		
231A	Ozonated-Biotreated	8.2	68	2	15				
231A		9.0	80			12	26		
231A	Acidified-Biotreatment	8.3	209	12	18	--	--		
231A	Steam Stripped Bottoms	1.0	466	60	75	--	--		
221A	Ozonated-Steam Stripped Bottoms	0.3	39[illegible]	180	72	--	--		
221A		0.5	350			75	95		
351A	Raw	11.7	59	9	33	--	--		
351A		12.0	56			--	3.5	0.3	

Breakthrough Data

Using data obtained from the multicomponent isotherm study, a continuous-flow carbon study was initiated using Monochem and Nuchar carbons. A continuous flow system consists of a series of carbon columns through which the water to be treated is pumped continuously until contaminant "breakthrough" occurs. Breakthrough is the point at which the contaminant concentration reaches an undesirable concentration. This method gives an accurate estimation of the large-scale operating capabilities of the activated carbon.

The laboratory pilot unit constructed was similar to the unit used in the first bench study. Two glass columns 2.54 cm in diameter, and 91.44 cm long, were constructed into the continuous-flow apparatus, as seen in Figure 12. One column supported the Monochem activated carbon, the other supported Nuchar. The process streams utilized in the isotherm experiments were used for these tests.

A glass wool plug was placed in the bottom of each column to trap any finely granulated carbon particles. All streams were filtered prior to being subjected to the continuous-flow system; however, a glass wool plug was placed at the top of each column to remove any particulate matter present after filtration. Teflon O-rings were evenly spaced in the carbon column to minimize channeling. The filtered feed was pumped to each column using one double-head, calibrated Masterflex pump and control unit. By using a tight-fitting rubber stopper at the top of each column, a pressure equivalent to the flow rate force of the pump was exerted on the feed. Although a free-flow system was desirable, some pressure was detectable depending on how tightly packed the column was.

The breakthrough curves generated in the initial phase of the project indicated a hydraulic loading of between 0.35 and 3.5 $l/min-m^2$ to yield satisfactory results. The lower loading gave the best adsorption data for the streams being studied; therefore, 0.7 $l/min-m^2$ was chosen to be the initial loading. This hydraulic loading was calculated to be approximately a 40 ml/min flow rate. Time of collection was approximately 11 min for every 500 ml sample. Results of the continuous flow study are listed in Table 65.

Regeneration

Regeneration was carried out on the 231A raw and 351A raw process streams. The procedure for regeneration was as previously set forth:

1. Wet carbon dried at 103°C and weighed.
2. Regenerated at 760°C for 2 hrs under steam.
3. Quenched, dried at 103°C and reweighed.
4. Weight loss calculated.
5. Continuous-flow study on regenerated carbon.

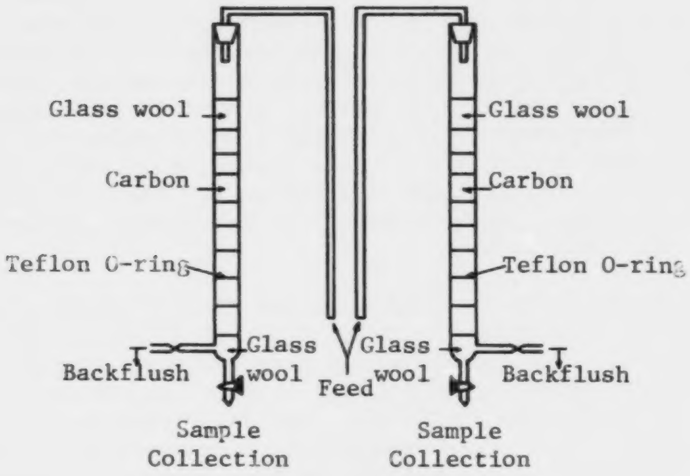
Glass wool
Carbon
Teflon O-ring
Backflush
Glass wool
Feed
Glass wool
Sample Collection
Glass wool
Carbon
Teflon O-ring
Backflush
Sample Collection

Figure 12. Continuous-flow apparatus.

TABLE 65. CONTINUOUS FLOW DATA

	231A TDI Raw		231A TDI Biotreat		231A TDI Acidified		231A TDI Ozonated, Biotreat		351A Aromatic Raw	
	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar
Initial Carbon Weight (g)	135.6g	154.4g	67.8g	67.8g	25.0g	25.0g	20.0g	20.0g	22.2g	21.8g
Volume at Breakthrough (Liters)	9.5	10.0	8.0	27.0	1.0	2.5	.5	1.0	15.0	16.5
Mg TOC Adsorbed/ g carbon	34.5	33.6	18.9	42.8	5.6	10.7	1.1	2.5	90.9	148.4

6. Analytical results, TOC, COD, BOD_5 (mg/1) were plotted versus volume (liters).

A composite list of data correlating activated and regenerated information is given in Table 66. Breakthrough curves are given in the Appendix.

Discussion of Results

After running the comparative continuous-flow study on Monochem and Nuchar carbons, definite conclusions were drawn about the adsorbing and regenerating ability of the Monochem activated carbon.

1. On all streams, Nuchar adsorbs at least 30 percent better than Monochem carbon--sometimes as high as 55 percent better.
2. It takes longer for breakthrough to occur for Nuchar than Monochem carbon.
3. Upon regeneration, Monochem has approximately a 50 percent weight loss, while that of Nuchar is rarely over 20 percent.
4. Monochem seems to retain its adsorbing ability after regeneration, while Nuchar tends to lose much of its ability.

TABLE 66. CONTINUOUS-FLOW DATA ON ACTIVATION AND REGENERATION PROCEDURE

Stream	231A TDI Raw		231A TDI Biotreated		231A TDI Acidified		231A TDI Ozonated,Biotreat		351A Aromatic Raw		231A Regenerated Raw		351A Regenerated Raw	
	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar	Monochem	Nuchar
Initial Carbon weight used	135.6g	154.4g	67.8g	67.8g	25.0g	25.0g	20.0g	20.0g	22.2g	21.8g	60.0	60.0	19.7g	19.7g
Volume at Breakthrough in Liters	9.5	10.0	8.01	27.01	1.01	2.51	.51	1.01	15.0	16.51	47.51	47.1	8.51	10.1
$\frac{\text{Mg TOC Adsorbed}}{\text{g carbon}}$	34.5mg	33.6mg	18.9mg	42.8mg	5.6mg	10.7mg	1.1mg	2.5mg	90.9mg	148.4mg	45.1mg	60.3mg	89.3mg	120.3mg
Weight Loss in Grams due to Regeneration	60.4g	28.2g	20.6g	9.9g	10.6g	10.2g	10.2	4.7	11.9	2.2	--	--	--	--
Percent Weight Loss from Initial Weight	48.4	18.2	30.3	14.6	42.4	40.8	51	23.5	53.6	10.0	--	--	--	--
Percent Gain or Loss $\frac{\text{Mg TOC}}{\text{gc}}$ after Regeneration											23.5 gain	44.2 gain	1.7 loss	18.9 loss

SECTION 7

SOLVENT EXTRACTION

As an integral part of EPA Grant No. S800773, "Development of Treatment and Control Technology for Refractory Petrochemical Wastes," solvent extraction was evaluated as an effective means to reduce organic contaminants in preselected process effluents. The waste streams were made available by eight participating industries in the Lower Mississippi River area. Inspection of the contaminants in the various process effluents led to a grouping of the wastewaters by manufacturing process:

1.	Ethylene dichloride	via	direct chlorination
2.	Ethylene dichloride	via	oxychlorination
3.	Perchloroethylene and 1,1,1-trichloroethylene	via	chlorination of ethylene dichloride
4.	Ethyl benzene	via	alkylation of benzene
5.	Toluene diamine	via	hydrogenation of dinitrotoluene
6.	Polyols	via	polymerization of ethyleneoxide
7.	Acetylene	via	combustion of methane
8.	Methylcellulose	via	propylene oxide

Four process effluent categories were considered for evaluation. Extraction process evaluations and subsequent field tests were based on the following considerations:

Stream No.	Type Contaminant	Discussion
221A	Halogenated hydrocarbon	Easy to solvent extract. Solvent selection dependent on residual in wastewater and its resulting need for further treatment.
351A	Aromatics	High dissolved solids. Aromatics could be solvent selective.
231A	Aromatic amines	Not too amenable to extraction.
231B	Polyols	Some detergent action which could inhibit solvent selectivity.

A three-point program was devised and carried out to determine if these process effluents were amenable to solvent extraction for contaminant reduction.

1. Laboratory development work on solvents selected for evaluation of the process effluents.
2. Demonstration unit design
3. Demonstration unit operations.

LABORATORY DEVELOPMENT ON SOLVENTS SELECTED FOR EVALUATION OF THE PROCESS EFFLUENTS

As previously discussed, the halogenated hydrocarbon contaminated process effluents were amenable to removal of organics by solvent extraction. The aromatic contaminated wastewater from the styrene process offered similar possibilities. Three separate process effluents were investigated on a laboratory scale for removal of trace organics by selective solvent extraction (Table 67).

TABLE 67. PROCESS EFFLUENTS

Stream Number	Type of Process Effluent
161A	Contaminated with chlorohydrocarbons from oxychlor process
221A	Contaminated with chlorohydrocarbons from oxychlor process
231A	Contaminated with aromatic amines

Stream 161A

This wastewater is from an ethylene oxychlorination process producing chlorinated solvents. The stream was analyzed first for gross parameters (Table 68). The results of these tests revealed some variation in the contaminant loadings of the wastewater from day-to-day operations. The process effluent was tested for organic compound removal with the kerosene and C_{10}-C_{12} petroleum solvents.

TABLE 68. INITIAL EVALUATION OF STREAM 161A

Parameter	Sample 1	Sample 2
pH	1.75	1.76
TOC (mg/1)	61.7	123
TOD (mg/1)	176	480
Cl^- (mg/1)	3240	4400
Acidity as $CaCO_3$ (mg/1)	3055	2431
Acidity as Chlorine (mg/1)	0.22	0.09

Conventional separatory funnel laboratory experiments were set up to determine the equilibrium conditions for contacting these solvents with this wastewater. The results of these tests are shown in Table 69.

TABLE 69. EXTRACTION OF STREAM 161A WITH C_{10}-C_{12} SOLVENT AND KEROSENE (Solvent to Wastewater Ratio 7 to 1)

Organic Compound	Influent (mg/1)	Kerosene Effluent (mg/1)	C_{10}-C_{12} Hydrocarbon Effluent (mg/1)
Vinyl Chloride	1	1	1
Ethyl Chloride	3	1	1+
Vinylidene Chloride	13	1	1
Dichloroethylene	49	2	1+
Chloroform	--	--	--
Ethylene Dichloride	320	--	16
Carbon tetrachloride	--	--	--
Trichloroethylene	24	6	5
Trichloroethane	75	2	3
Perchloroethylene	14	2	1
Tetrachloroethane	148	7	6
Pentachloroethane	10	2	--
Unknown	6	2	1
Total	663	43	36
Percent Removed		94	95
Solubility of Solvent in water in mg/1	--	30	20

These two solvents offer excellent possibilities to utilize in the field test on the larger continuous demonstration unit. There were a number of advantages in using these two solvents:

1. Excellent selectivity for the specific organic compounds present.
2. Low solubility in the wastewater after extraction.
3. Availability at a reasonable cost.
4. Post-biodegradability and non-toxic characteristics.
5. The boiling point enables separating the extracted organics by distillation.

The C_{10}-C_{12} hydrocarbon fraction is produced in a petrochemical operation. This paraffin-based material is extensively used in detergent manufacture and is used as the starting material conversion to a substituted fatty acid. Because of this specific use, it is manufactured at a rather wide temperature range. The initial boiling point could cause some problems in distilling the organics from the solvent.

The subsequent field test results showed that these two solvents could be used effectively for removal of chlorinated hydrocarbons from process effluents.

Stream 221A

This wastewater is also from an ethylene oxychlorination process producing primarily EDC. The stream was analyzed for gross parameters (Table 70). Initial evaluations of two samples from this process effluent indicated that there was little variation between the processes. The analysis of the organic components averaged between the two samples is shown in Table 71.

TABLE 70. INITIAL EVALUATION OF STREAM 221A

Parameter	Sample 1	Sample 2
pH	--	1.29
TOC (mg/1)	--	866
COD (mg/1)	1383	1309
TOD (mg/1)	2253	1940
Cl^- (mg/1)	6000	6800
Acidity as $CaCO_3$ (mg/1)	7565	8233
Suspended Solids (mg/1)	9.7	8.0
Volatile Suspended Solids (mg/1)	0.9	0.9

TABLE 71. ORGANIC COMPONENTS IN STREAM 221A

Component	Concentration (mg/l)
Methyl Chloride	2
Chloroform	683
Ethylene Dichloride	8331

Since this wastewater contained primarily ethylene dichloride, solvents other than kerosene and C_{10}-C_{12} hydrocarbons were evaluated. Examination of the previous solvent work on stream 161A indicated that the petroleum fractions were effective in removing EDC from the process effluent. Several solvents were selected which were considered both selective and easily separated from the extracted organics by distillation. Table 72 presents the results of these tests with the solvents selected.

TABLE 72. SOLVENT EXTRACTION OF WASTE STREAM 221A

			TOC (mg/l)	
Solvent	Solute Volume (ml)	Solvent Volume (ml)	Before Extraction	After Extraction
Carbon Disulfide	25	100	357	370
	50	100	357	378
	100	100	357	350
1,1,2,2-Tetrachloroethane	25	100	357	485
	50	100	357	560
	100	100	357	762
Pentane	25	100	357	406
	50	100	357	508
	100	100	357	521
Cyclohexane	25	100	357	430
	50	100	357	378
	100	100	357	346
Freon	25	100	357	378
	50	100	357	393
	100	100	357	362

As an initial evaluation, the TOC values of the influent and effluent after extraction tests were used to indicate the potential value of the selected solvents. Results of this series of extraction tests were disappointing. With the exception of two values, the effluent TOC was higher than the TOC in the influent. (This is because the low molecular weight solvents are more soluble in water than the higher, longer chain hydrocarbons.) The selectivity of these solvents for specific organics in the wastewater was not checked. It was apparent that since the initial TOC was not being reduced, the wastewater would have to be treated by other means to remove contaminants in order to comply with existing effluent standards.

Stream 231A

This stream was a wastewater from the manufacture of toluene diisocyanate. The primary organic constituent was toluene diamine, the actual organic composition was complex due to the many side reactions which occurred in the process sequence. The gross characteristic parameters are presented in Table 73. It was decided to evaluate the extraction efficiency of several selected solvents utilizing TOC as the analytical means of indicating solvent selectivity. These results are shown in Table 74.

TABLE 73. INITIAL EVALUATION OF STREAM 231A

Parameters	Concentration
pH	11.6
TOC (mg/1)	687
COD (mg/1)	663
TOD (mg/1)	4388
Phenol (mg/1)	6.6
Cl^- (mg/1)	2500
Alkalinity as $CaCO_3$	2408
Suspended Solids (mg/1)	11.8
Volatile Suspended Solids (mg/1)	3.1

As in the case of process effluent 221A, this wastewater was not amenable to extraction with the various solvents selected. The only solvent which showed any selectivity was 1,1,2,2-tetrachloroethane. Removal of organics, as indicated by TOC measurements, was approximately 50 percent. This reduction would not be sufficient and further treatment of the wastewater would be required.

DEMONSTRATION UNIT DESIGN

The initial investigations indicated that the organics in the wastewater would be in the range of 1,000 to 10,000 mg/1. A concentration of 9,000 mg/1 was used as the basis of calculations. The distribution coefficient was assumed to be 30 for these determinations.*

Design Calculations for Demonstration Unit

$X_f = 9{,}000 \qquad X_n = 27$

$X_n/X_f = 27/9{,}000 = 0.003$

Solvent to process effluent ratio assumed to be 10

$B = 0.10 \times 0.75 = 0.075$

$A = 1.0 \times 1.0 = 1.0$

$E = 30 \times 0.075 = 2.25$

To accomplish such an extraction result would take from 10 to 15 theoretical stages. The amount of removal of trace organics by solvent extraction

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*Preliminary designs furnished by Texas A & M.

TABLE 74. SELECTED SOLVENT EXTRACTION OF STREAM 231A

Solvent	Solute Volume (ml)	Solvent Volumn (ml)	TOC (mg/l) Before Extraction	After Extraction
Carbon Disulfide	Partially soluble in wastewater.			
Dibutyl Phthalate	Did not separate readily from wastewater.			
Dodecanol	25	100	4320	4687
	50	100	4320	4221
1,1,2,2-Tetrachloroethane	25	100	4320	3288
	50	100	4320	1974
	100	100	4320	2089
Pentane	25	100	4320	4320
Cyclohexane	25	100	4320	4348
	50	100	4320	3992
Freon ($H_2C_2Cl_2F_2$)	25	100	3704	3388
	50	100	3704	3521
	100	100	2704	3829
Octane	25	100	3704	4056
	50	100	3704	3948
	100	100	3704	3969
Dodecane	25	100	3704	4497
	50	100	3704	3658
	100	100	3704	3858
1,4-Dichlorobutane	25	100	3704	6390
	50	100	3704	7489
	100	100	3704	15359
1,2,3,4-Tetrachlorobutane	40	100	3704	3498
	100	100	3704	5171
C_{10}-C_{12} Paraffins	25	100	3704	3715
	50	100	3704	4152
	100	100	3704	3877

determines the number of stages required to achieve the desired level of organics in the extracted aqueous process effluent. The quantity of throughput determines the diameter of the extraction equipment.

Final Demonstration Unit Design and Construction

A liquid-liquid extraction pilot unit capable of processing 3.8 liters of wastewater per minute with a solvent rate of 0.76 l/min was designed. Specifications for the design were as follows:

Wastewater Specifications	
Dissolved inorganics	5% hydrochloric acid; others negligible
Dissolved organics	Primarily, ethylene dichloride concentrations from 1000 - 9000 mg/l, boiling point 57°C
Flow	3.8 l/min
Acidity	5% HCl
Solvent Specifications	
Solvent	C_{10}-C_{12} paraffin based oil, boiling range 204 to 315°C
Flow	0.76 l/min
Column Specifications	
Extraction column	0.01 m diameter, 3.5 m tall
Stripper	0.005 m diameter, 2.25 m tall
Materials of Construction	
Main vessels	Hastelloy-C, glass, etc.
Seals, gaskets, etc.	Viton®, Teflon®, polypropylene

Chem-Pro Equipment Corporation of Fairfield, New Jersey, was contracted to fabricate the liquid-liquid extraction and solvent recovery components of the pilot unit. From preliminary design drawings, Chem-Pro developed working drawings of the solvent extraction and solvent recovery systems (Fig. 13).

Equipment--

The liquid-liquid extraction system was a Karr reciprocating plate extraction column which was 3 m in height and 10 cm in diameter. There were 65 plates mounted on a central shaft reciprocated by a drive mechanism located above the column. A 1.25-cm amplitude of reciprocation was set by adjusting the length of the crank arm. The speed of reciprocation was a function of the solvent particle size, solvent distribution throughout the column, and the flow rates of the aqueous feed and solvent. Materials of construction were a Hastelloy-C shaft, borosilicate glass pipe, and T.F.E.

The stripper was 2.25 m in height, made of 0.05 m schedule 10 Hastelloy-C pipe with a 0.15 m section of Hyperfill packing. Steam was injected through

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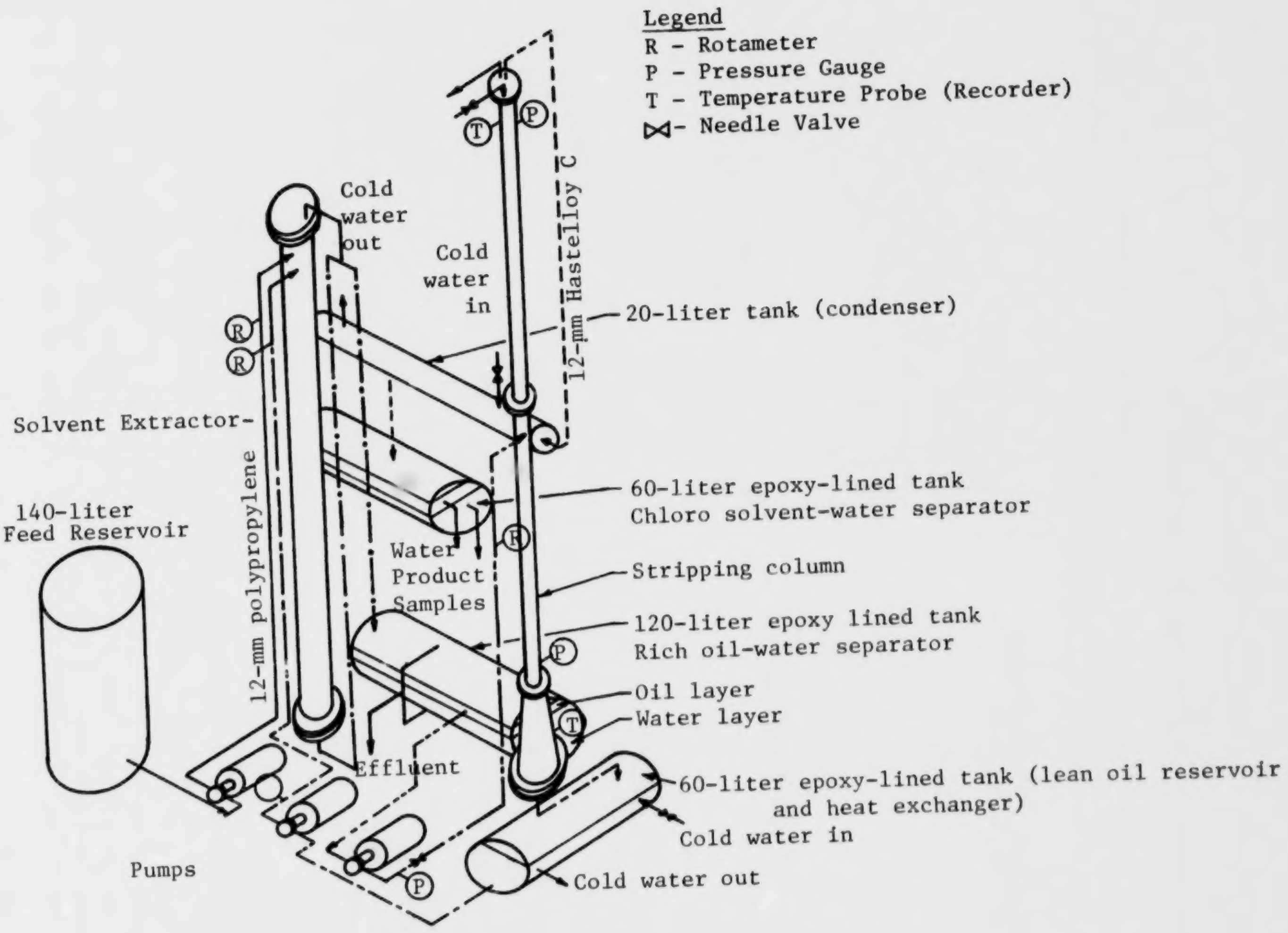
Legend
R - Rotameter
P - Pressure Gauge
T - Temperature Probe (Recorder)
⋈- Needle Valve
Cold water out
Cold water in
12-mm Hastelloy C
20-liter tank (condenser)
Solvent Extractor-
60-liter epoxy-lined tank
Chloro solvent-water separator
140-liter Feed Reservoir
12-mm polypropylene
Water Product Samples
Stripping column
120-liter epoxy lined tank
Rich oil-water separator
Oil layer
Water layer
Effluent
60-liter epoxy-lined tank (lean oil reservoir and heat exchanger)
Cold water in
Pumps
Cold water out
R
R
R
P
P
P
P
T
T

Figure 13. Solvent extraction pilot plant (operational concept).

a 0.02 m nozzle, 0.53 m above the bottom of the column. The variable-flow self-priming pump, made by Flotect, Inc., can lift water 6-7.5 m and discharge between 0-18 l/min. The body and impeller were made of a chemical-resistant epoxy plastic and the shaft, cone, and backplate were made of Hastelloy-C. The power requirements for the 1/3 HP explosion-proof motor were 230V, single-phase current.

DEMONSTRATION UNIT OPERATIONS AT PLANT SITE

Based on the laboratory evaluations of solvent selectivity, it was decided to set up the field trials utilizing a petroleum kerosene fraction as the first solvent and a C_{10}-C_{12} paraffin based on petroleum fraction as the second solvent (Table 75).

TABLE 75. PROPERTIES OF KEROSENE AND C_{10}-C_{12} SOLVENT

Solvent	Kerosene	C_{10}-C_{12}
Boiling Range (°C)	149-260	174-216
Specific Gravity	0.862	0.75
Viscosity (cP @ 24°C)	1.1	1.1

Solvent characteristics of kerosene-type distillates vary according to the amounts of paraffins, aromatics or naphthas present. These classes of compounds vary depending on the source of crude from which they are manufactured. The kerosene base used for these tests contained more paraffin and naphtha based products than aromatics. Its solvent properties were more like the C_{10}-C_{12} based material. The C_{10}-C_{12} petroleum fraction is obtained by selective fractionation, adsorption or extraction of a paraffin petroleum fraction. Both solvents were readily available at a reasonable price.

The demonstration unit was moved to the process effluent stream 161A and set up for the trial runs. It was planned to utilize the kerosene-based material first, followed by the C_{10}-C_{12} solvent.

Kerosene-Diesel Oil Trials

Kerosene-diesel solvent was run to find an optimum water-to-solvent ratio. Fifteen extraction runs were made with kerosene-diesel oil with water-to-oil ratios varying from 3.7:1 to 18.3:1. Table 76 shows total chlorinated organics removed. The effects of kerosene-diesel oil solvent on removal of the three main contaminants (1,1,2-trichloroethane, EDC, and 1,1,2,2-tetrachloroethane) from stream 161A are presented in the Appendix. An approximate ratio of 5.5:1 (water:solvent) gave the maximum percent removal of 94 to 96 percent of the chlorinated organics.

The percent of the chlorinated organics removed increased as the water-to-solvent ratio decreased, except for the runs on October 11 and December 11. No explanation can be given for the deviation of these two runs from the norm. Runs on December 10 and 16 were very high in chlorinated

TABLE 76. CHLORINATED ORGANICS REMOVED WITH A KEROSENE-DIESEL SOLVENT

Date	Solvent Flow (1/min)	Water Flow (1/min)	Chlorinated in (mg/1)	Organics Out (mg/1)	Amount Removed (mg/1)	Percent Removed	Ratio $\frac{H_2O}{\text{Solvent}}$
10/23/74	0.205	3.76	1,591	514	1,077	68	18.3:1
10/11/74	0.205	2.81	907	81	826	91	13.7:1
10/11/74	0.205	1.86	715	101	614	86	9.1:1
10/31/74	0.288	2.62	609	92	517	85	9.1:1
11/21/74	0.205	1.86	334	62	272	81	9.1:1
11/25/74	0.205	1.14	1,043	58	985	94	5.5:1
12/11/74	0.205	1.14	701	129	572	82	5.5:1
12/16/74	0.205	1.14	3,689	143	3,546	96	5.5:1
12/04/74	0.205	1.14	382*	224*	158	41	5.5:1
01/06/75	0.205	1.14	654†	33†	621	95	5.5:1
12/2-3/74#	0.205	1.1 & 0.8	771#	63#	700	92	3.7:1 & 5.5:1
12/10/74	0.205	0.76	2,757	122	2,635	96	3.7:1
12/17/74	0.205	0.76	907	45	862	95	3.7:1
01/07/75	0.204	0.76	413†	20†	393	95	3.7:1

*The solvent was reused before it was transferred to the stripper to determine if the oil was loaded with chlorinated organics. EDC and three other components increases in the raffinate while seven components decreased at varying degrees.

†An uncontaminated solvent was used in this run to compare results with the recycled solvent.

#The lab combined samples from 12/2 and 12/3 when H_2O:Oil ratios were 3.3:1 and 6.0:1, respectively.

organics (2,757 and 3,689 mg/l, respectively), with both runs having 96 percent removal. These results indicated that further concentration of the contaminated waste streams would increase the efficiency of removing chlorinated organics from water.

On January 6, an uncontaminated solvent was used to compare results with the recycled solvent. The total chlorinated organics in the raffinate (effluent water) were 33 mg/l for a water-to-oil ratio of 5:1. This is 25 mg/l lower than the best results obtained using the recycled solvent. Any increase in the solvent or steam flow caused overhead entrainment. A laboratory analysis of the solvent indicated that there was 1.24 percent to 0.23 percent Cl_2 in the unstripped solvent and 0.02 to 0.03 percent Cl_2 after the solvent had been stripped (Table 77).

TABLE 77. EFFICIENCY OF PILOT STEAM STRIPPER FOR REMOVAL OF CHLORINATED ORGANICS FROM EXTRACT

	Tested for Total Cl_2 in the Kerosene-Diesel Oil Extract		
Date	Before Stripper	After Stripper	Percent Removed
11/4/74	0.23% Cl_2	0.02% Cl_2	91
12/3/74	0.74% Cl_2	0.02% Cl_2	97
12/17/74	1.24% Cl_2	0.03% Cl_2	98

C_{10}-C_{12} Solvent

A water-to-solvent ratio of 16.4:1 gave the maximum number of theoretical stages and 93.8% removal of the chlorinated organics (Table 78). The number of theoretical stages increased as the water-to-solvent ratio increased up to 16.4:1. At 20.0:1, problems with the column flooding and poor dispersion of the solvent caused the percent removed to drop to 72.3 and 76.6. The C_{10}-C_{12} paraffin solvent was not recycled and no tests were run to determine the amount of chlorinated organics in the extract.

To estimate the solubility of the C_{10}-C_{12} solvent in water, a comparison between the GC analyses was made. The TOC analyses were run four days to one week after the samples were taken. (With this delay, errors in the comparison of GC carbon and TOC are possible.) The influent TOC should not be smaller than the influent GC carbon. For the runs on 3/24, 3/26 and 3/27, the influent GC carbon is larger than the influent TOC. These runs were not included in determining the solubility of the solvent (C_{10}-C_{12}) in the raffinate. A summary of all runs is shown in Table 79, and is accompanied by a sample calculation. Comparing the TOC analysis and the GC analysis, the solubility of the solvent in the raffinate was estimated to be 12-27 mg/l.

TABLE 78. CHLORINATED ORGANICS REMOVED WITH A C_{10}-C_{12} PARAFFIN SOLVENT

				Chlorinated Organics[a]			Total Organic Carbon[b]	
Date	Ratio (H_2O:Solvent)	Water Flow (1/min)	Solvent Flow (1/min)	In (mg/1)	Out (mg/1)	Percent Removed	In (mg/1)	Out (mg/1)
3/20	5:1	1.23	0.27	148.4	3.2	97.8	58	37
3/17	6.5:1	1.71	0.27	184.6	3.0	98.4	73	48
3/25	8:1	2.13	0.27	164.9	1.8	98.9	59	38
3/21	10:1	2.66	0.27	297.4	6.6	97.8	76	39
3/24	16.5:1	4.37	0.27	266.6	16.5	93.8	54	75
3/26	20:1	5.32	0.27	713.8	197.6	72.3	173	86
3/27	20:1	5.32	0.27	672.0	157.3	76.6	75	87

[a] Analyzed by gas chromatograph

[b] Analyzed by TOC analyzer Beckman 915

Economic Evaluation for Contaminant Removal of Stream 161A by Solvent Extraction

The following criteria were established as a basis to develop the cost-benefit ratio for utilizing solvent extraction removal of trace organics in the process effluent.

Basis

1. 331 days per year and/or 8,000 hr per year was the annualized time the unit would be in operation.

2. Straight-line depreciation of capital equipment over the first 10 years of operation.

3. Interest on capital investment at 8 percent.

4. 532 l/min of process effluent as feed to the extractor.

5. The halogenated hydrocarbon organics which are extracted will be steam-stripped and recycled back to the the process.

6. The concentration of halogenated hydrocarbon in the process effluent was 1000 mg/l.

7. Recovered product value was equal to 13.4¢/kg.

Capital Cost-

To arrive at a capital cost estimate for installing the equipment necessary to extract the wastewater and steam strip the resulting organic rich solvent, conventional techniques of major equipment pricing were employed with appropriate factoring.

Equipment Cost Estimate

	Equipment	
1.	Feed storage tank	$ 8,000
2.	Extractor column 0.91 x 9.1 m	50,000
3.	Stripper column 2.54 cm x 7.62 m	10,000
4.	Stripper column condenser	2,000
5.	Stripper column exchanger	3,000
6.	Stripper column cooler	3,000
7.	Pumps	10,000
8.	Instruments	10,000
9.	Piping, valves and fittings	12,000
10.	Intermediate drums and tanks	13,000
11.	Miscellaneous equipment	15,000
	Subtotal	$136,000
	Total Installed Cost	315,000

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TABLE 79. DETERMINATION OF C_{10}-C_{12} PARAFFIN SOLVENT SOLUBILITY

Date	Ratio H_2O:Solvent (liter/liter)	Influent TOC (mg/1)	Influent GC Carbon (mg/1)	Effluent TOC (mg/1)	Effluent GC Carbon (mg/1)	Solubility of Solvent in H_2O (mg/1)
3/20	5.0:1	58	32	37	1	12
3/17	0.5:1	73	38	48	1	14
3/25	8.0:1	58	36	38	1	18
3/21	10.0:1	76	62	39	2	27
3/24	16.5:1	54	57	75	4	--
3/26	20.0:1	173	179	86	48	--
3/27	20.0:1	75	148	37	36	--

SAMPLE CALCULATION RUN OF 3/17

Component	Influent (mg/1)	(Times)	Carbon	(Equals)	Influent GC Carbon (mg/1)
VC	0.7	x	.38436	=	.27
EC	0.1	x	.37235	=	.04
VDC	19.7	x	.24780	=	4.38
Trans	28.5	x	.24780	=	7.06
Cl_2	44.4	x	.24780	=	11.00
EDC	4.5	x	.24274	=	1.09
TCE	30.9	x	.18007	=	5.08
Tri	27.7	x	.18283	=	5.06
Per	14.3	x	.14486	=	2.14
U-Tetra	4.1	x	.14312	=	.59
S-Tetra	6.8	x	.14312	=	.29
Penta	2.4	x	.11875	=	38.47

Effluent GC Carbon = 0.34 mg/1
Influent TOC = 73 mg/1
Effluent TOC = 48 mg/1

There possibly could be compounds in the influent water which are not shown by the GC analysis that do contain organic carbon. Assume all the organic carbon not shown by the GC analysis in the influent is not extracted and remains in the effluent.

Influent TOC	/3 mg/1
-GC Carbon	-38 mg/1
Influent Organic Carbon not shown by GC Analysis	35 mg/1
Effluent TOC	48 mg/1
-GC Carbon	-1 mg/1
	47 mg/1
-Influent Organic Carbon not shown by GC Analysis	-35 mg/1
Organic Carbon from the Solvent	12 mg/1
Organic Carbon from the Solvent	12 mg/1
Percent Carbon in the Solvent (C_{11})	.34615
Solubility of the Solvent in Na_2Sr	14 mg/1

Operating Cost--

The items which go into the operational cost of such a processing unit are listed below. The manpower allowance was arbitrarily set at a total of three men for an around-the-clock operation. This is actually less than a full-man per shift, and it is assumed he could perform other duties associated with the major process for a portion of his shift duties.

Operating Cost

Steam consumption 350,000#/yr @ \$3.00/1,000#	\$ 1,000
Electricity 15 KWH @ 2.5¢/KWH	4,000
Labor (3 men @ \$15,000/man)	45,000
Supplies and chemicals (1.5% capital)	5,000
Solvent (7600 liters/yr @ \$0.26/liter)	2,000
Supervision (2.0% of capital)	6,000
Maintenance and materials (8% of capital)	25,000
Total	\$88,000

Fixed Cost--

The two significant fixed costs applicable to this operation are depreciation and interest on the capital. The actual capital required would have to be larger than needed for equipment and installation to cover start-up expenses, working capital, and the general and administrative corporate business expenses allocated to each cost center. These costs are outlined below.

Fixed Costs Per Year

1.	Depreciation - 10 years straight line	\$31,500
2.	Interest - 10 years at 8% (Averaged over a 10-year period)	14,000
3.	Start-up expenses	15,000
4.	Working capital	15,000
5.	General and administrative, insurance and taxes	12,000
	Total	\$88,000

Recovered Product Credit--

The average concentration of ethylene dichloride in the process effluent which was evaluated on the bench unit varied from 300 to 3,000 mg/l. An average value of 1,000 mg/l was taken for purposes of determining a recovered product credit. Plant value was assumed to be 13.2¢/kg.

Removable Organics By-Product Credit

Flow	254,000,000 kg/yr
Recoverable organics in process effluent	1,000 mg/l
Recoverable organics	254,000 kg/yr
Recoverable organics @ 13¢/kg	33,000

Cost-benefit Value of Solvent Extraction of Stream 161A--

The amount of ethylene dichloride and chlorinated solvents which would generate 532 l/min of process effluent would have an annual capacity of approximately 227,000,000 kg/yr. The cost analysis (below) indicates that the cost to treat the process effluent would be approximately 0.066¢/kg. Solvent extraction as an initial in-plant treatment represents an amortized cost of less than 1 percent of the product sales price. It should be recognized that this process effluent would have to be included in the final plant effluent treatment system. That portion of final treatment cost would have to be allocated on a proportional basis to this process effluent for a final cost analysis.

Cost Per Year	
Variable costs (operations)	$ 88,000
Fixed costs (depreciation, etc.)	88,000
Subtotal	$176,000
Recovered Credit	33,000
Total Annual Cost	143,000
Cost/liter of Water Treated	$ 0.0007

SECTION 8

STEAM STRIPPING

The removal of trace organics from process effluents by steam stripping offers distinct advantages for a number of organic processes in the chemical industry. When the trace organics are volatile and make up the bulk of the contaminant in the process effluent, this unit operations approach is a viable means of reducing wastewater loadings for a number of reasons.

1. Direct injection of steam eliminates reboiler cost.
2. Azeotropic boiling points of a number of organic compounds with water permits their removal with a minimum of aqueous boilup.
3. Regulation of the amount of water taken overhead with the organic contaminants could create a two-phase system, permitting recycle of the organic layer to the process and refluxing of the water layer.
4. Wastewater contaminants are controlled in the immediate process area with maximum product recovery.
5. Final plant effluent treatment load and resulting cost are minimized.

The most frequently used rule for relating the composition of the vapor phase of an equilibrium liquid mixture to pressure and temperature is Dalton's law. It states that the total pressure of a system is equal to the sum of the partial pressures of the individual components present.

$$\text{Total Pressure} = P_1 + P_2 + P_3 + \ldots . P_n$$

According to Dalton's law, partial pressure is the pressure that would be exerted by a component if it were alone at the same molal concentration that it is in the mixture.

The organics present in a process effluent frequently form a constant boiling concentration with the aqueous phase. Such a mixture can be carefully distilled so that the minimum water required for this azeotrope will be taken in the overhead. The resulting overhead system could then be separated into an organic layer and an aqueous layer containing the excess organics originally present in the contaminated process effluent.

By utilizing Dalton's law, an aqueous effluent can be tested to see if steam stripping will effectively remove trace organics. The contaminated water can be heated to the effective boiling point of the organic in the presence of the water. Careful regulation of the water taken overhead with the organic will permit the separation of the overhead into an organic-rich phase and an aqueous-rich phase. The organic phase can be recycled to the process and the aqueous phase utilized as reflux.

As in all processes, this unit operations approach is less applicable to certain trace organic contaminated process effluents.

1. If some of the organics in the effluent do not respond to this unit operations approach, the resulting stripper bottoms may still contain significant amounts of BOD_5 and TOC.

2. The combination of stream stripping secondary treatment may not be cost effective.

3. Recycle of stripper overhead to the process may not be possible due to the miscibility characteristics of the organics. Disposal of the concentrated organic wastewater may present a greater problem than the dilute stream.

4. Recycle of the stripper overhead may present long-term process problems even if the organics form an immiscible layer. Buildup of impurities through recycle could cause the main process to produce undersirable trace impurities.

The evaluation of stream stripping for the removal of organics from wastewaters therefore requires a careful analysis of a specific industrial operation. The 23 process effluents considered for the applicability of steam stripping are listed in Table 80. There were four major groups of organic components in the process streams.

1. Wastewater containing chlorinated hydrocarbons--The 17 effluents in this group contained 2 basic contaminants: (1) soluble organics which are volatile and steam strip individually or as an azeotrope; and (2) soluble organics which are not readily volatile and difficult to steam strip.

2. Wastewaters containing aromatic hydrocarbons--There were two process effluents in this category: (1) quench waters from an ethylene cracking unit and (2) wash waters from an ethylbenzene-styrene plant. The quench water contained too wide a boiling range of hydrocarbons to be effectively steam stripped. The wash water had primary aromatics in the benzene, ethylbenzene, and styrene cateogry, and was selected for evaluation by steam stripping.

3. Wastewaters containing aromatic amines and related organics--Water solubility precluded these impurities from being concentrated by stripping or reboiling.

TABLE 80. CODED PROCESS WASTEWATER STREAMS

	Stream 1D	Major Contaminant
1	011A001	Halogenated Hydrocarbons
2	011B001	Halogenated Hydrocarbons
3	011C001	Halogenated Hydrocarbons
4	041A001	Halogenated Hydrocarbons
5	041BC01	Halogenated Hydrocarbons
6	041C001	Halogenated Hydrocarbons
7	041D001	Aromatics and Organic Oxides
8	041E001	Halogenated Hydrocarbons
9	041F001	Halogenated Hydrocarbons
10	041G001	Methyl Cellulose and Hydroxyethers
11	081A001	Halogenated Hydrocarbons
12	081B001	Halogenated Hydrocarbons
13	081C001	Halogenated Hydrocarbons
14	131A001	Aromatics (Quench)
15	161A001	Halogenated Hydrocarbons
16	161B001	Halogenated Hydrocarbons
17	161C001	Halogenated Hydrocarbons
18	221A001	Halogenated Hydrocarbons
19	221B001	Halogenated Hydrocarbons
20	221C001	Halogenated Hydrocarbons
21	231A001	Aromatics and Amines
22	231B001	Polyols and Oxides
23	351A001	Aromatics

4. Wastewaters containing polyols and polyhydroxy-type organics--The high-boiling, water-soluble polyols were not amenable to removal by steam stripping.

Each of the process effluents was completely characterized before any decisions were made as to the steam stripping tests which would be applied to the selected streams. Individual samples were collected for each stream which were representative of the process conditions, and specific tests were conducted to establish all of the component parameters. Details of the tests performed on each process stream are given in Tables 81 and 82.

LABORATORY BENCH-SCALE STRIPPING COLUMN

General Design Conditions

After the initial evaluations of the process streams, a pilot stream stripping system was designed. The demonstration unit (Figure 14) was based on a feed flow rate of 3.8 l/min. The column was made from a 5.08 cm piece of Derokane, with an overall length of 3.67 m. Packing for the column was pall rings made from polypropylene. Feed to the system was

TABLE 81. STREAM CHARACTERIZATIONS

Stream ID	COD (mg/1)	TC (mg/1)	pH	Flow (1/min)	Alkalinity $CaCO_3$ (ppm)	Acidity $CaCO_3$ (ppm)	Chlorides Cl (ppm)
011A	3,678	1,665	12.2	76-228	16,600	0	18,113
011B	1,112	712	1.5	57-152	0	29,254	1,988
011C	615	1,703	11.2	288-418	4,840	0	6,664
041A	1,764	1,638	11.7	342-456	1,060	0	2,662
041B	30	250	2.9	342-456	0	135	408
041C	454	13	2.6	342-456	0	241	762
041D	325	69	6.9	1520-2280	30	10	7
041E	10,752	2,576	5.8	342-456	375	8	6
041F	18	54	10.5	342-456	325	0	418
041G	23,198	7,409	10.6	114-228	--	--	28,617
081A	6	60	10.6	76-114	1,180	0	1
081B	100	17	1.4	76-114	0	2,680	1,909
081C	390	67	12.1	76-114	12,635	0	9,685
131A	1,060	273	9.5	114	220	0	119
161A	1,040	1,843	7.7	76-190	304	10	6,140
161B	418	148	0.9	57-114	0	0	10,587
161C	6,279	4,390	<0.1	38-95	0	0	77,112
221A	15,100	9,022	0.1	57-114	0	102,312	116,127
221B	11,280	10,250	<0.1	38-76	0	269,392	170,289
221C	6,080	5,840	12.7	19-38	31,800	0	46
231A	10,680	1,310	9.7	38-76	1,475	0	14
231B	2,562	821	11.9	57-95	1,140	0	32
061A	463.6	479	11.9	76-152	2,060	0	147

TABLE 82. SOLUBLE ORGANIC STREAM CHARACTERIZATION

Soluble Organics	011A (mg/l)	011B (mg/l)	011C (mg/l)	041A (mg/l)	041B (mg/l)	041C (mg/l)	041D (mg/l)	041E (mg/l)	041F (mg/l)	081A (mg/l)	081B (mg/l)	081C (mg/l)	161A (mg/l)	161B (mg/l)	161C (mg/l)	221A (mg/l)	221B (mg/l)	221C (mg/l)	231A (mg/l)	231B (mg/l)	351A (mg/l)
Methyl Chloride	T	1.0	736.0	0-40	2.4	2.0			200.0		3.0	2.0	3.0	2.0	14.0	2.0	0.2		Toluene diamine and isocyanate	Polyols and solvent	
Ethyl Chloride	19.7	T	0.9	0-30	T				T					6.5	2.7		3.8	21.4			
Vinylidene Chloride	1.0		0.8			0.3		2.0	5.7	0.1	1.0	0.1	10.0	6.5	56.8						
Trans 1,2-Dichloroethylene						0.1							0.1	19.7	327.4	1.3					
Cis 1,2-Dichloroethylene		T	6.0			0.1				10.0		0.5	7.0	64.0	546.3		1.1				
Chloroform	2.5	0.1	25.0			0.2		0.2	15.6.			1.0	23.0			683.0	0.96				
EDC	6974.0	2858.0	5755	9122	6.0	6.0		2.0	3.3	6.0	42.0	2.0	200.0	310.0	1077.6	8331.0	9238	54.8			
Carbon Tetrachloride						5.0				1.0	2.0	8.0						0.21			
Trichloroethylene						3.0				202.0	3.0	84.0	6.0	25.5	109.6						
1,1,2-Trichloroethane			17.0										40.0	29.6			53.6				
Perchloroethylene										7.0	7.0	20.0	14.0	10.4							
Tetrachloroethane										306.0											
Toluene							2.0														1.2
Benzene							11.6														5.65

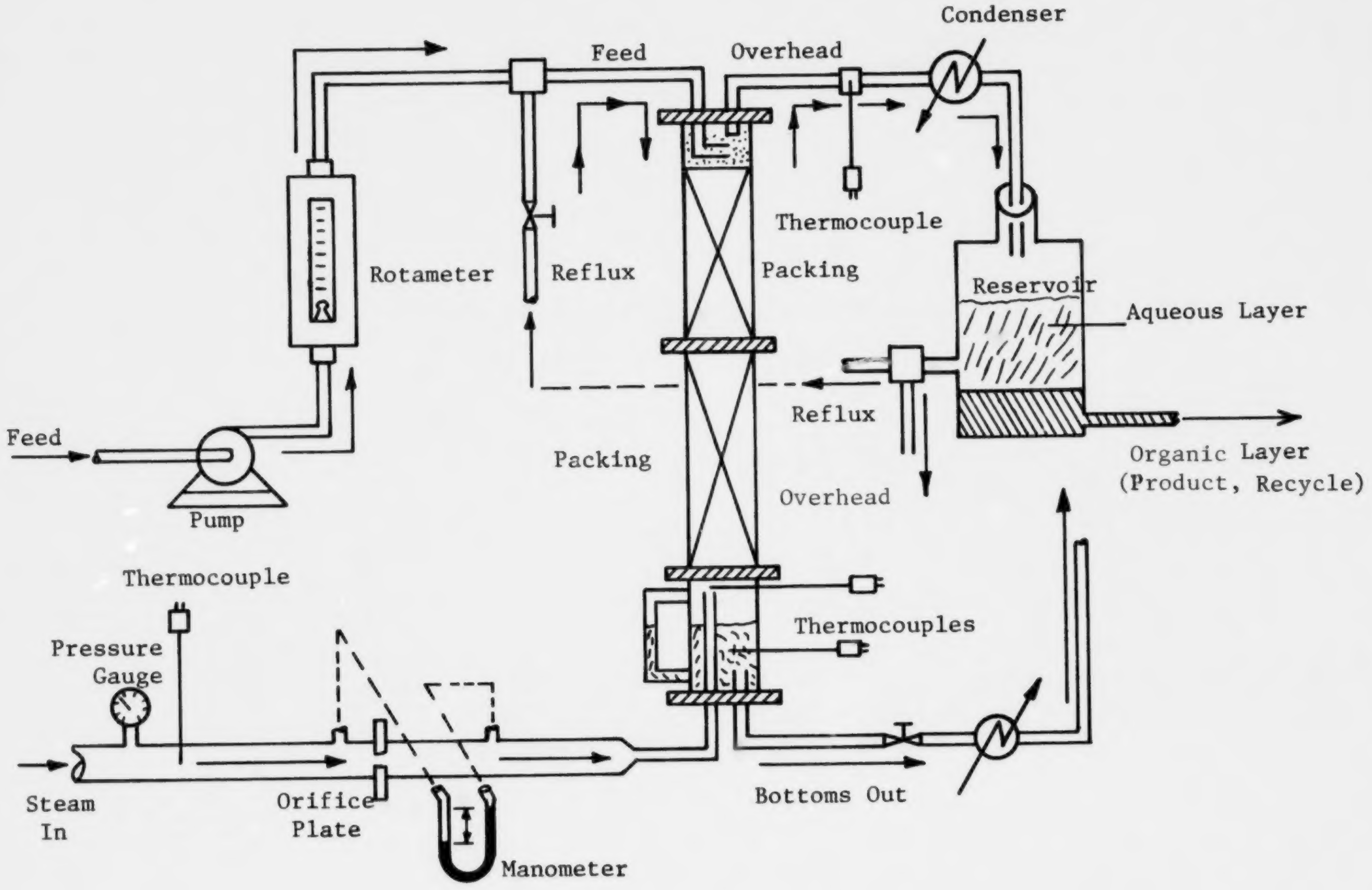
Condenser
Feed
Overhead
Thermocouple
Rotameter
Reflux
Packing
Reservoir
Aqueous Layer
Feed
Reflux
Organic Layer
(Product, Recycle)
Pump
Packing
Overhead
Thermocouple
Thermocouples
Pressure
Gauge
Steam
In
Orifice
Plate
Manometer
Bottoms Out

Figure 14. Model of pilot steam stripper (GSRI - New Orleans).

measured through a calibrated rotameter using a peristaltic pump for flow continuity. Steam was from an on-line boiler which serviced the main building. Steam feed was preset with a needle valve and measured through a calibrated orifice.

To minimize process losses, the bottom and overhead products were condensed in a refrigerated bath. All flow meters and orifices were precalibrated under process conditions. The discharge of the steam pipe was disconnected and the steam condensed by use of the refrigerated bath. The condensate was collected and weighed over a period of time; the results were checked against the pressure drop through the orifice system.

Experimental Procedures

The following procedures were used to collect the samples on which the data in this report were based.

Overhead--

The overhead samples from the steam stripper were composited hourly from 6 samples taken every 10 min in a graduated cyclinder. An average hourly rate was calculated and recorded. A grab sample was then collected in a 150-ml brown bottle and analyzed for EDC content.

Bottoms--

The bottoms from the steam stripper were monitored through a sight glass and valve on the column. An average flow rate for the bottoms was calculated from samples collected for 1 min in a graduated cylinder. Samples of the bottoms for EDC analysis were collected in the same manner as for the overhead samples.

Feed--

The feeds for the pilot steam stripper were received in 210-liter polypropylene-lined drums and fed to the stripper by a Masterflex pump. The feed rate was measured at 1-min intervals and feed samples for EDC analysis were taken at the end of each day.

Steam Rate--

Steam rate to the pilot stripper was measured by a U-type manometer across an orifice plate.

STEAM STRIPPING TRIALS

Experimental Operations and Results

Halogenated Hydrocarbon Contaminated Wastewaters--

There is a great deal of similarity among the organic components present in the wastewaters from this industry segment. Three representative effluents were selected. A program was developed to evaluate steam stripping and its effectiveness in removing trace contaminants.

1. Steam stripping of stream 221A with a detailed analysis of influent and effluent from the stripper, including individual organic component analysis.

2. Steam stripping of stream 011C with analysis of the influent and effluent for broad TOC parameters. In addition, the composition of ethylene dichloride would be measured during the stripping operation. (Since this EDC usually is the major organic component in the process effluents, it was felt that if the EDC were removed, then other organics present would be reduced to a minimum.)

3. Steam stripping of stream 161A with monitoring of the operation utilizing only gross parameters such as TOC and BOD_5.

4. Evaluation of the three pilot unit tests to see if any additional data are needed to design a commercial-size steam stripping unit.

Steam Stripping of Stream 221A

To ensure adequacy and uniformity of process wastewater, several drums were collected and delivered to the pilot unit area. The system was run continuously while varying specified process conditions. Samples were collected from the feed source over one day's operation to check the uniformity of the feed. The data indicated that the organics could be easily removed and that minimum overhead would yield the desired results. Further, the quantity of overhead should be kept to a minimum if the overhead were to separate into an organic-rich phase and a water-rich phase. The results of the test program are given in Table 83.

Discussion of Results--

Variations in the data became evident in comparison between the individual test runs. Test 2 allowed 2.8 percent of the feed to be taken overhead. The amount of 1,2-dichloroethylene removed was only 2.3 percent. The material balance for this organic was not as good as it should be; the real conditions for organic removal were much better than the results indicated, since it was apparent that volatile organics had escaped undetected.

In the third test, the amount of overhead was increased to 5.1 percent. As expected, the amount of organics removed increased to 90.74 percent. The amount of 1,2-dichloroethylene in the bottoms decreased to 14.8 mg/1, indicating a 90 percent removal for this component. The process material balance for this organic was still not within the expected experimental range.

In the final tests, the overhead was decreased to a quantity similar to Tests 1 and 2, and the results of the first run were checked. The results of this test were promising. With a lower overhead, the organics removed amounted to 85.2 percent of the organics in the influent. The amount of 1,2-dichloroethylene in the overhead was much higher, indicating that this organic is so volatile that it was difficult to collect even with refrigeration. Special efforts were made during this run to obtain maximum overhead. An excellent material balance was obtained for several of the individual components, though the overall material balance was not good.

The last two tests were conducted by holding the overhead fairly constant and reinjecting the overhead water phase at varying amounts.

TABLE 83. STEAM STRIPPING OF STREAM 221A*

Test	1	2	3	4	5
Volume (ml/min)					
O.H.	5.76	7.05	12.75	4.3	13.5
Btms	350	281.25	302.5	305	275
Percent					
O.H.	2.3	2.82	5.10	2.3	2.5
Steam (ml/min)	44.98	53.1	50.8	59.7	59.7
Temperature (^oC)					
O.H.	103	102	104	104	103
Btms	104	103	104	104	103
Column Pressure (Btm/Top)	1.0/1.0	1.0/1.0	1.0/1.0	1.0/1.0	1.0/1.0
Mass Balance Efficiency (%)	+17.08	-4.80	+2.09	+3.099	-6.845
Stripper Col. TOC	(mg/1)				
Btm	256	292	593	241	243
O.H.	10446	10462	4766	4519	9806
Feed	645	668	645	785	636
Reflux Ratio	--	--	--	1.411	0.8511
TOC Removal (%)	37.3	55.8	37.7	32.9	83.3

*O.H. = Distillate or overhead.
Btms = Column effluent or bottoms.
Negative mass balance efficiencies indicate less material into system than leaves system.
Column feed = 250 ml/min for all tests.

Refluxing the overhead water phase increases the efficiency of the stripping operation but necessitates increasing the amount of steam for stripping.

The removal of organics varied from 80 to 84 percent. These numbers compare favorably with the previous runs. The data from these five runs indicated that up to 90 percent of the individual organics can be removed through the use of steam distillation. It appears that additional height of column packing is necessary to maximize the reduction of organics in the stripper bottom.

Contaminant Loading of the Stripper Bottoms--

The feasibility of the steam stripping of the halogenated hydrocarbon contaminated wastewater had been demonstrated. The next step was to evaluate the residual impurities of the stripper bottoms. Samples of each of the previous runs had been retained for TOC analysis. This parameter was felt to be a good measure of organics removed in the stripping operation and of the residual contaminants in the bottoms. The results of these tests are shown in Table 84. The data indicate a consistent stripper performance. With the exception of one run, the TOC removal varied between 56 and 69 percent.

Since the biological data had indicated that this residual was reducible by this process, a combination of these two processes would appear to offer a feasible treatment sequence.

Steam Stripping of Stream 011C

Stream 011C is from an oxychlor operation manufacturing ethylene dichloride. An analysis of this stream is shown in Table 85. EDC is the principal organic contaminant in the wastewater.

TABLE 85. CHARACTERIZATION OF STREAM 011C PROCESS EFFLUENT

COD (mg/l)	615
TC (mg/l)	1703
pH	11.2
Flow (l/min)	380
Alkalinity as $CaCO_3$ (mg/l)	4840
Chlorides Cl (mg/l)	6564
Vinylidene Chloride (mg/l)	2.8
Dichloroethylene (mg/l)	8.5
Chloroform (mg/l)	28.2
Ethylene Dichloride (mg/l)	1913.0
Trichloroethylene (mg/l)	36.3
Tetrachloroethylene (mg/l)	5.2
Total Organics (mg/l)	1999.2

A number of runs were made on the pilot unit, monitoring the total organic carbon and determining the concentration of EDC in the influent and effluent streams. A summary of these data is shown in Table 86.

TABLE 84. STEAM STRIPPING OF STREAM 221A COMPONENT ANALYSIS OF FEED OVERHEAD AND BOTTOMS$^+$ (ppm)

		2.3% OH*		2.8% OH		5.1% OH		1.4:1 Reflux to OH Ratio 2.3% OH		0.9:1 Reflux to OH Ratio 2.5% OH	
	Feed	OH	BTM**	OH	BTM	OH	BTM	OH	BTM	OH	BTM
Vinylidene Chloride	61.49	124.4	32.8	--	--	111.2	0	--	--	179.9	0
Dichloromethane	800.89	3511.8	114.1	3277.0	89.5	2736.5	175.6	1183.0	296.3	5159.9	131.7
1,2-Dichloroethylene	1583.3	350.8	373.7	269.7	1255.4	465.0	14.8	1320.9	16.1	679.9	0
Chloroform	140.3	1185.1	0	882.4	0	838.3	0	412.3	0	1124.3	64.7
1,1,1-Trichloroethane	50.92	--	--	--	--	--	--	--	--	173.4	41.6
Ethylene Dichloride	1593.0	4383.5	42.20	4105.5	64.5	4731.5	43.1	3654.5	38.6	5541.3	436.4
Trichloroethylene	--	640.8	34.2	567.0	0	627.4	22.7	640.8	37.2	644.5	0
Chloral	693.18	1213.0	171.9	1163.6	177.1	1185.5	172.6	2332.3	464.3	2301.6	434.4
1,1,2-Trichloroethane	14.14	24.6	0.19	34.0	0	76.5	0	42.4	0	66.1	0
Perchloroethylene	14.89	--	6.8	50.2	0	--	--	--	--	9.6	0
1,1,1,2-Tetrachloroethane	512.8	189.8	0	393.8	0.84	22.7	0	25.8	0.5	392.5	1.6
1,1,2,2-Tetrachloroethane	14.9	14.9	32.7	121.7	49.5	444.4	78.4	8.7	0	24.2	0.1
		85.24% Removal in Bottoms		70.13% Removal in Bottoms		90.74% Removal in Bottoms		84.4% Removal in Bottoms		79.9% Removal in Bottoms	

+Feed to column was 250 ml/min for all tests

*OH = distillate as % of feed

**Btm= bottom, effluent from column

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TABLE 86. PILOT PLANT EVALUATION FOR STEAM STRIPPING OF STREAM 011C

						Ethylene Dichloride			TOC		BOD_5	COD		TOD
Run Number	Feed ml/min	Overhead ml/min	Bottoms ml/min	Reflux ml/min	Steam ml/min	Feed mg/l	Overhead mg/l	Bottoms mg/l	Feed mg/l	Bottoms mg/l	Botoms mg/l	Feed mg/l	Bottoms mg/l	Bottoms mg/l
1	395	11.4	410	--	69	1,716	8,835	65	--	--	--	--	--	--
2	300	16.0	340	--	69	1,612	10,446	65	--	--	--	--	--	--
3	300	10.0	335	--	59	1,612	9,937	65	--	--	--	--	--	--
4	300	5.2	330	--	52	1,612	7,765	65	--	--	--	--	--	--
5	390	16.0	420	--	75	1,962	10,470	65	--	--	--	--	--	--
6	390	11.0	410	--	69	1,962	11,253	65	--	--	--	--	--	--
7	335	6.4	400	--	58	1,204	7,364	65	--	--	--	--	--	--
8	335	12.1	425	--	65	1,204	16,184	65	--	--	--	--	--	--
9	335	20.0	350	--	72	1,204	11,294	65	--	--	--	--	--	156
10	370	9.8	420	--	65	2,111	8,143	65	--	--	--	--	--	158
11	370	5.0	410	--	55	2,111	21,595	65	--	--	--	--	--	76
12	245	55.0	290	--	87	10,734	16,278	0.3	--	--	--	--	--	70
13	245	34.0	270	--	65	10,734	15,655	1.0	--	--	--	--	--	73
14	245	19.0	255	--	46	12,900	16,698	1.0	--	--	--	--	--	64
15	245	52.0	290	32	87	12,900	14,853	1.0	--	--	--	--	--	188
16	290	30.0	340	--	80	8,042	13,880	1.0	--	--	--	--	--	169
17	290	11.0	345	--	65	8,042	13,377	1.0	--	--	--	--	--	161
18	290	36.0	380	25	83	8,042	14,876	1.0	--	--	--	--	--	188
19	370	18.5	410	--	71	7,403	14,012	1.0	--	--	--	--	--	164
20	400	31.5	425	--	76	7,403	12,433	1.0	--	--	--	--	--	195
21	400	16.6	410	--	69	7,403	12,821	1.0	--	--	--	--	--	210
22	400	6.0	410	--	69	7,403	13,411	1.0	--	--	--	--	--	--
23	400	13.8	475	--	77	--	--	5.3	801	129	--	--	--	--
24	500	12.5	530	--	84	--	--	1.0	801	102	--	--	--	--
25	280	10.9	350	--	50	--	--	1.0	801	109	--	--	--	--
26	380	19.4	450	--	77	5,600	14,800	1.0	739	115	--	--	--	--
27	380	12.3	390	--	72	5,600	13,900	1.0	739	120	--	--	--	--
28	390	21.7	460	--	84	5,640	19,629	43	710	185	--	--	--	--
29	390	10.8	490	--	80	5,640	21,419	3.6	740	191	--	--	--	--
30	390	33.0	470	22	87	5,640	16,065	4.0	740	166	--	--	--	--
31	260	15.7	300	--	56	5,189	16,409	3.7	732	160	--	--	--	--
32	290	9.1	350	--	65	5,762	18,100	5.7	765	69	--	--	--	--
33	290	35.1	391	27	84	5,762	19,294	1.0	531	67	61.4	518.7	125.2	--
34	335	10.3	394	--	60	5,084	16,956	1.0	531	30	74.9	518.7	146.3	--
35	335	42.0	418	32	84	5,084	17,180	1.4	531	57	66.6	518.7	118.1	--
36	350	18.3	400	--	80	1,463	6,587	6.0	531	121	77.9	518.7	200.3	--
37	225	12.0	279	--	55	1,247	6,838	9.2	531	111	72.6	518.7	233.2	--
38	225	47.8	324	36.3	77	1,247	5,230	9.5	531	111	68.1	518.7	199.5	--
39	240	14.1	309	--	56	1,426	6,030	7.0	531	125	--	518.7	--	--
40	250	10.8	271	--	56	1,426	5,935	9.3	512	125	--	409.2	--	--
41	250	42.3	285	33.3	77	1,457	4,925	6.1	512	106	--	409.2	--	--
42	280	14.2	301	--	65	1,457	7,106	8.5	512	91	116.0	409.2	--	--
43	280	57.1	366	42.9	102	1,457	5,895	19.4	512	69	110.0	409.2	--	--

During the experimental tests, the feed, overhead reflux and steam rate were varied sufficiently to establish optimum operating conditions. An examination of the continuous operation of the steam stripping column revealed that it was possible to obtain good material balances. Total input to the column was represented by the feed stream and the injected steam. Effluent was represented by the overhead and bottoms. Average deviation from the column material balance was less than 10 percent.

While obtaining these data on stream 011C, the process effluent was field sampled on several occasions. Sampling at different intervals pointed up the variation in organic concentrations of this wastewater.

Good material balances were obtained during the experiment, but mass balances for the measured quantities of EDC in the influent and effluent were disappointing. Although a refrigerated system was used to collect the overhead and bottoms samples, it was apparent that some vaporization did occur.

Considerable effort was made in the initial tests to achieve equilibrated operating conditions prior to examining the stripper bottoms for residual organic contamination. Levels of TOC, BOD_5, TOD, and COD in the stripper bottoms were determined. Removal of these parameters is illustrated in Table 87. From these data, it would appear that the TOC level in the final effluent can be reduced to an average value of approximately 100 mg/l. The COD values are somewhat higher, and BOD_5 somewhat lower.

Some minor oxidation products apparently are present in this wastewater as in stream 221A. However, the products are not as prevalent and should present no problems.

Discussion of Results--

The EDC content of the wastewater used as feed to the stripper column varied from 1,247 to 12,900 mg/l. Over this range, it was possible to reduce the EDC in the stripper bottoms to less than 1 mg/l. The range of EDC in the bottoms corresponded to a TOC value of 100 mg/l, a BOD_5 value in the 75 mg/l range, COD value in the 150 to 200 mg/l range, and a TOC value in the 100 to 200 mg/l range.

As in stream 221A, there was a soluble organic present in stream 011C which was not steam stripped. This organic has been identified as chloral, which is a halogenated ethylene compound with a hydroxyl group attached to one of the carbon compounds. The addition of this hydroxyl group seems to enhance the biodegradability of the compound.

Steam stripping of stream 011C produces a wastewater quite low in the measurable parameters of TOC and BOD_5.

Steam Stripping of Stream 161A

The principal product of this process was ethylene dichloride. Wastewater characteristics are listed in Table 88. The analysis of this process effluent indicated that it had fewer contaminants at an overall

TABLE 87. ANALYSIS OF STREAM 011C
(Concentrations in mg/1)

	BOD	COD	TOC	TOD	Alka-linity	Chlor-ides	Cu	Fe	pH
Bottom R33	61	125.2	67	112	1310	4370	0.24	0.23	12.0
Bottom R34	75	146.3	30	135	1450	5280	0.11	1.38	12.0
Bottom R35	66.6	118.1	55	129	1350	4930	0.17	0.67	11.9
Bottom R36	78	200.3	122	152	1350	5440	0.96	0.31	11.9
Bottom R37	73	233	111	181	1430	5330	0.13	4.01	
Bottom R38	68	199.5	111	213	1200	4700	0.11	2.41	11.9
Bottom R39		169	125	221	1390	5220	0.07	0.63	
Bottom R40		186	125	251	1635	5310			11.9
Bottom R41		170	106	249	1400	5310			11.8
Bottom R42	116	183	91	253	1684	6660	<0.09	0.22	
Bottom R43	110	170	69	221	1425	5480	<0.09	0.07	11.8
Bottom R44			116	274	2514				11.44
Bottom R45			117	253	2324				11.45
Bottom R46	106		108	197	2426				11.6
Bottom R47	85		110	217	2518		<0.09	1.42	11.35
Bottom R49			86	468	4918				11.95
Bottom R50			87	542	4950				12.1
Feed R43-39		518.7	531		1915	700	0.13	2.57	12.0
Feed R40-43		409	512	5190	2247	6210			
Feed R44-60		539	491	4445	2250	7700			

TABLE 88. CHARACTERIZATION OF STREAM 161A PROCESS EFFLUENT

COD	1040 mg/l
TC	1843 mg/l
pH	7.7
Flow	189.3 l/min
Alkalinity (as $CaCO_3$)	304 mg/l
Chlorides	5140 mg/l
Vinylidene Chloride	2.6 mg/l
Dichloroethylene	8.1 mg/l
Chloroform	22.0 mg/l
EDC	25.7 mg/l
Trichloroethylene	7.1 mg/l
Trichloroethane	34.2 mg/l
Perchloroethylene	13.8 mg/l
Tetrachloroethane	39.7 mg/l
Total Organics	153.2 mg/l

lower concentration than the two wastewaters previously evaluated. Therefore, steam stripping of this effluent provided data on unit operation at a lower concentration range. A minimum of test runs provided the data for this wastewater. Results for this stream are shown in Table 89.

Discussion of Results--

The EDC content of the wastewater used as feed to the stripper column varied from 1,247 mg/l to 12,900 mg/l. Over this range, it was possible to reduce the EDC in the stripper bottoms to less than 1 mg/l. This range of EDC in the bottoms corresponded to a TOC value on the order of 100 mg/l, a BOD_5 value in the 75 mg/l range, COD value in the 150 to 200 mg/l range and a TOD value in the 100 to 200 mg/l range.

As for wastewater from streams 221A and 011C, chloral was present in stream 161A and was not steam stripped. The only explanation is that the addition of the hydroxyl group enhanced the solubility of this type of compound. Steam stripping of this process effluent produces a wastewater quite low in the measurable parameters of TOC and BOD_5.

Steam Stripping Aromatic Contaminated Wastewaters for Stream 351A

Two primary process effluents are contaminated with the various organics utilized in the manufacture of ethylbenzene: the overhead from the benzene drying column and the wash water from the alkylation intermediate products. In the production of styrene, sources of process effluent are the chilled brine tank overflow and the vacuum jet collection water. The process effluents from the ethylbenzene-manufacturing operations are combined at battery limits and become the major process effluent from an ethylbenzene-styrene plant. Other sources of wastewater are minor and intermittent.

TABLE 89. TESTS RUN ON STREAM 161A

Run Number	Feed ml/min	Overhead ml/min	Bottoms ml/min	Reflux ml/min	Steam ml/min	TOC (mg/l) Feed	TOC (mg/l) Overhead	TOC (mg/l) Bottoms	Mass Balance Efficiency (%)	Percent TOC Removal
1	276	7.8	388	--	54	150	64	142	+19.8	1.2
2	255	13.5	321	--	50	158	115	139	+ 9.7	3.9
3	235	11.4	340	8	65	24	88	16	+17.1	17.8
4	245	5.3	290	--	51	16	84	15	- 0.8	11.4
5	243	9.4	272	15.4	--	99	132	76	--	5.2

The stream characteristics of process effluent 351A are listed in Table 90.

TABLE 90. STREAM CHARACTERIZATION OF STREAM 351A

Item	Units	Concentration
COD	mg/l	239
TOC	mg/l	49
pH		9.4
Chlorides	mg/l	315
Benzene	mg/l	5.7
Toluene	mg/l	1.2
Ethylbenzene	mg/l	8.5
Xylene	mg/l	0.6
Styrene	mg/l	0.7

Stream stripping of this wastewater should yield a wastewater with only the inorganics and suspended solids as impurities. This was verified with actual stripping tests. A number of runs were made with the aromatic rich wastewater as feed. The results of these tests are summarized in Table 91.

Discussion of Results--

Some variation in the feed composition, as measured by TOC, was noted throughout the series of tests. At the higher feed contaminant loading, the removal efficiency was better.

Sources of benzene could be a cause of these process contaminants. Benzene is derived from two major raw material sources: by-product recovery in the coking industry and solvent extraction of petroleum-based products. Each source generates different trace contaminants in the final product. The coke-based product usually includes xylenes, phenolics, and related substituted compounds boiling in the same range. These compounds can be present in the benzene feed stack in extremely small quantities and be magnified several times in the final alkylate wash water.

Design Specifications for Commercial-Size Unit

A commercial-sized unit for installation at the plant site of stream 011C was designed. A site visit was made to get an overview of the physical layout of the existing operations. Consultation with company participants established design conditions.

To initiate the design, a complete material balance was established for the process of each element of the influents and effluents: feed rate, overhead rate, bottoms rate, and steam rate. All conditions for the final commercial unit are given in Table 92. A material balance flow sheet is shown in Figure 15 Process and instrument design conditions are included.

TABLE 91. STEAM STRIPPING OF STREAM 351A

Run Number	Feed ml/min	Overhead ml/min	Bottoms ml/min	Reflux ml/min	Steam ml/min	TOC (mg/l) Feed	TOC (mg/l) Overhead	TOC (mg/l) Bottoms	Mass Balance Efficiency	Percent TOC Removal
1	250	10	207.5	--	54.7	315	65.0	24.0	+4.2	92.4
2	250	13.8	290.0	--	63.9	2416	98	118.0	-3.2	--
3	250	3.0	317.5	--	59.7	20.2	193	15.4	+3.5	23.8
4	258	11.5	312.5	15.0	53.1	67.2	83.3	45.1	+4.2	32.9
5	255	13.4	343.8	6.7	36.7	26.5	93.7	20.8	+18.3	21.5
6	252	6.5	338	--	--	90.0	147	40.0	--	55.5
7	250	8.2	342	--	--	80.0	280	46.0	--	79.4
8	255	7.5	452	--	--	58.0	209	37.0	--	36.2
9	261	14.0	380	--	--	155.0	737	14.0	--	98.1

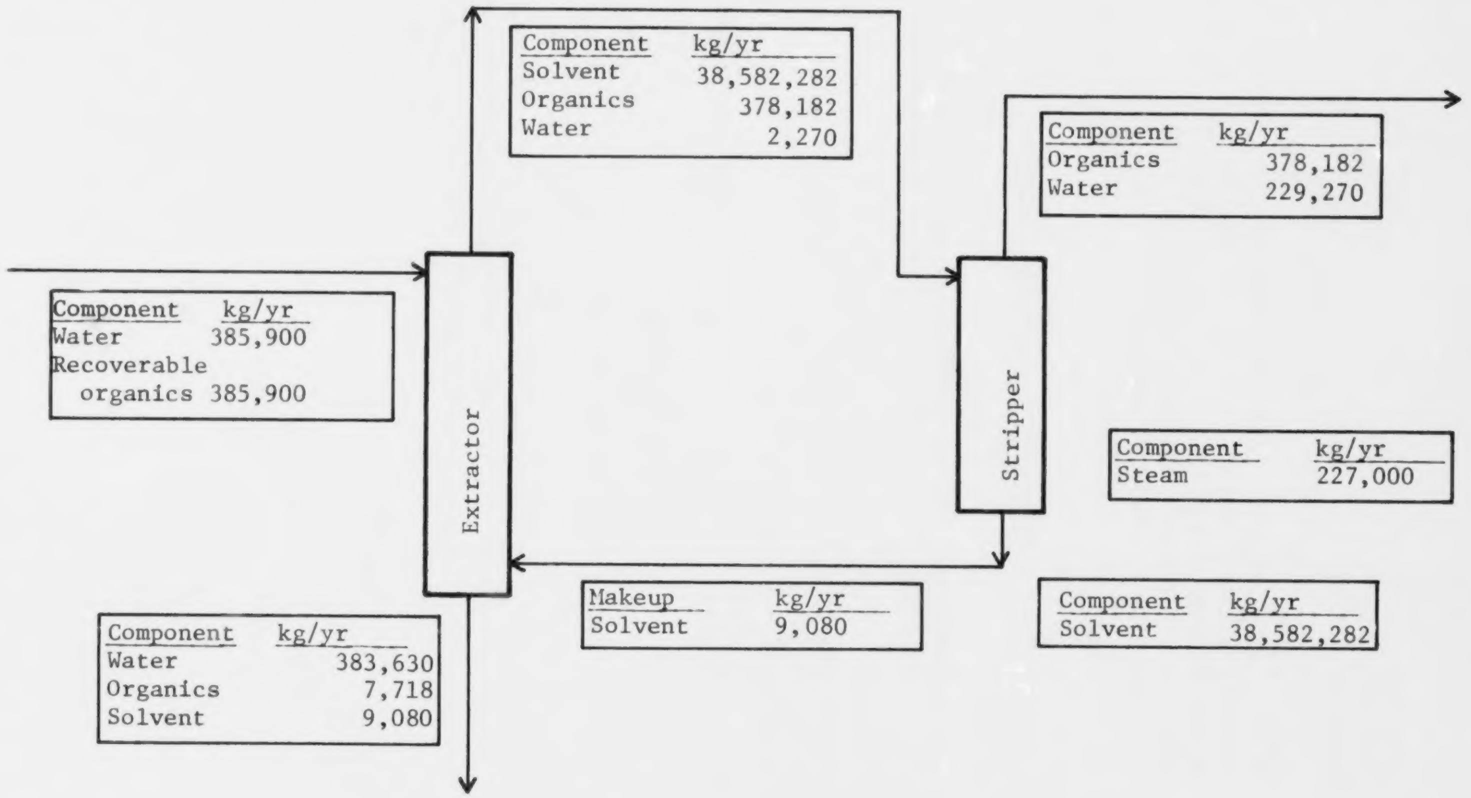

Component kg/yr
Solvent 38,582,282
Organics 378,182
Water 2,270
Component kg/yr
Organics 378,182
Water 229,270
Component kg/yr
Water 385,900
Recoverable organics 385,900
Extractor
Stripper
Component kg/yr
Steam 227,000
Component kg/yr
Water 383,630
Organics 7,718
Solvent 9,080
Makeup kg/yr
Solvent 9,080
Component kg/yr
Solvent 38,582,282

Figure 15. Material balance, process and instrument flowsheet.

TABLE 92. DESIGN PARAMETERS COMMERCIAL UNIT FOR STREAM 011C

Feed rate (l/m)	530
Feed rate (kg/hr)	32,000
Organics (kg/hr)	135
Overhead product (kg/hr) - 5% of Feed	1,600
Feed Preheat (°C)	93
Packing ring diameter (cm) (Pall Rings)	4
Stripper bottoms (kg/hr)	32,500
Stripper steam (kg/hr)	2,300
Ethylene dichloride in bottoms (kg/hr)	0.45
Ethylene dichloride in bottoms (mg/l)	13

Economic Evaluation of Steam Stripper Operation with Recycle of Recovered Organics

The following criteria were set as a basis for economic evaluation of steam stripping of a halogenated hydrocarbon contaminated wastewater from an economic standpoint.

1. 331 days/yr and/or 8,000 hr/yr.
2. Straight-line 10-yr depreciation.
3. Interest on capital investment at 8 percent with 10-yr payout.
4. 532 l/min process condensate treatment.
5. Overhead rate based on 5 percent of feed.

Capital Cost--

Conventional techniques of major equipment pricing and factoring were employed to arrive at a capital cost estimate of installing the equipment. Operational costs were based on the material balance and applied economic factors appropriate for this facility.

Equipment Cost Estimate

	Equipment	Cost
1.	Feed storage tank	$ 8,000
2.	Stripping column (packed)	28,000
3.	Feed pre-heater - 90 m^2 @ $380/$m^2$	35,000
4.	Condenser - 18 m^2 @ $380/$m^2$	7,000
5.	Separator drum	3,500
6.	Pumps (feed, oil layer, aqueous layer)	7,800
7.	Assorted piping	10,000
	Total	$99,000
	Total Installed Cost	$250,000

Operating Cost	Cost/Year
Steam Consumption ($6.60/1000 kg @ 2,250 kg/hr)	$120,000
Electricity (50 KW @ 2.5¢/KWH)	11,000
Labor (3 men @ $15,000/man)	45,000
Supplies & Chemicals (1.5% Capital Investment)	4,000
Supervision (2.0% of Capital Investment)	5,000
Maintenance & Materials (8.0% of Capital Investment)	20,000
Total	$205,000

Fixed Cost--

Two significant fixed costs are applicable to an economic evaluation of this operation: depreciation and interest on the capital. In addition to equipment installation, start-up expenses, working capital, and general corporate business expenses, contribute to the total capital requirement outlined below.

Fixed Cost Per Year

Depreciation - 10 year Straight line	$25,000
Interest - 10 years @ 8 percent	11,000
Start-up Expenses	10,000
Working Capital	10,000
General and Administrative, Insurance and Taxes	10,000
Total	$66,000

Recovered Product Credit--

The average concentration of ethylene dichloride in the process effluent evaluated on the bench unit varied from 1200 mg/l to over 10,000 mg/l. An average value of 5,000 mg/l was used to determine a recovered product credit. Plant value was assumed to be 13.24¢/kg.

Ethylene Dichloride Recovered Product Credit

Total Effluent = 31,780 kg/hr EDC
159 kg/hr ECD = 1,336,000 kg/yr.
EDC value @ 13.24¢/kg = $177,000

Cost-Benefit Value of Steam Stripping of Stream 011C--

The following comparisons were made to evaluate recovery and recycling of organics on the basis of in-plant treatment cost.

Cost Per Year

Variable Costs (operations)	$205,000
Fixed Cost (depreciation, etc.)	66,000
Total	$271,000
Recovered Credit	$177,000
Total Annual Cost	$ 94,000
Cost Per Liter of Water Treated	$ 0.00041

The amount of ethylene dichloride which would generate 532 l/min of process effluent would have an annual capacity of approximately 227,000,000 kg/yr. The above cost analysis indicates that the cost of EDC produced would be approximately 0.057¢/kg. Present EDC product value at plant site is approximately 22¢/kg. Steam stripping as an initial in-plant treatment represents an amortized cost of less than 1 percent of the product sales price, and removes over 99 percent of the organics present.

SECTION 9

OZONATION

INTRODUCTION AND PRINCIPLES OF OZONATION

Chemical oxidation has the potential for removing from wastewater organic materials which are resistant to other treatment methods. In many cases, these refractory materials are toxic to biological systems. The desirable characteristics of a chemical oxidant are that it be easily and economically available and that it not contribute secondary pollutants to the waste stream. Ideally, the oxidative process will result in the formation of nonpolluting gaseous products; carbon dioxide, water, etc. Practically, complete oxidation is difficult to achieve for most systems; the cost of treatment increases exponentially as complete oxidation is approached. In most cases, fragments of the original species remain and must not contribute to the waste stream contaminant load or must be amenable to further treatment.

Ozone is one of the strongest and purest oxidants available. Unlike other oxidants, it can be generated as needed on-site. Ozone has been used for years to purify, deodorize, and disinfect drinking water in Europe, and has more recently been used in the wastetreatment area to oxidize cyanide and phenolic wastewaters. Two types of reactions can occur with ozone as an oxidant. One is an electrophilic attack by ozone and the other an ozone-initiated oxidation in which ozone serves as the reaction initiator and oxygen is the principal reactant.

In a gas-liquid reaction such as the ozonation of industrial wastewaters, one or more of the reactants must pass through an interface between the phases to react. The overall relationship between mass transfer and the reaction kinetics must be studied to identify the controlling regime. Once the proper regime is identified, an appropriate reactor may be specified. Reactor types range from a bubble column for use with a slow reaction controlling to a packed column for mass transfer controlled reactions. A stirred tank reactor was chosen for this study as it can simulate a bubble column and approach the interfacial areas of a packed column by varying the agitation.

OBJECTIVES

The major objective of the ozonation study was to determine if ozonation would be feasible as a pretreatment for biorefractory wastes prior to biooxidation. (The high costs of ozone generation would probably make complete oxidation impractical.) Ozonation was performed on toluene diisocyanate (TDI), ethylene glycol, styrene monomer, and ethylene dichloride wastewaters. The effects of solution pH, temperature, and ozone mass transfer on the oxidation rate were evaluated in a stirred tank reactor. The reactor was operated in the semi-batch mode, continuously sparging gas into a constant volume of wastewater.

MATHEMATICAL MODEL DEVELOPMENT

A mathematical model was developed and used with experimental data to determine the reaction rate constants, volumetric mass-transfer coefficient, and the proper reaction regime for the ozone-styrene gas-liquid reaction. The model accounts for mass transfer of ozone into the liquid phase from the gas phase, ozone decomposition, and reaction with styrene and its reaction products. The model was developed from a macroscopic view of the reaction system promoted by Prengle and Barona (4). This procedure is based on a combination of Fick's law of diffusion and a material balance for each component in both phases over the entire reactor system. This can be expressed as

$$\frac{dC_j}{dt} = k_L a(C_{je} - C_j) - r_j \qquad (1)$$

where C_j is the concentration of component j, C_{je} is the concentration of component j at equilibrium, k_L is the liquid-phase mass-transfer coefficient, a is the interfacial area, and r_j is the reaction rate of component j.

The macroscopic view is illustrated in Figure 1 with a plot of the ozone concentration in the liquid phase as a function of time. In the absence of a liquid reactant, the ozone is absorbed exponentially to its solubility limit. This concentration profile of ozone in the liquid phase can be found by equating r_j to zero and solving Equation (1):

$$C_B = C_{Be}\ (1-e^{-\phi t}) \qquad (2)$$

where C_B is the ozone concentration in the liquid phase, C_{Be} is the equilibrium ozone concentration in the liquid phase, and ϕ is the combination of the volumetric mass-transfer coefficient and the ozone decomposition rate constant (5).

The ozone concentration profile is shown for the three most frequent gas-liquid reaction regimes in Figure 16. After an injection of liquid reactant at time zero, the ozone concentration immediately drops to zero if the reaction is instantaneous. The result is a truly mass transfer limited system as depicted by line 1. A quasi-equilibrium concentration is reached if mass transfer is controlling with a slow reaction (line 2). The ozone concentration will remain at the solubility limit if the system is reaction rate controlled (line 3). The reaction regime was identified for each compound ozonated by conducting a material balance on each component and comparing the data to the theoretical plot.

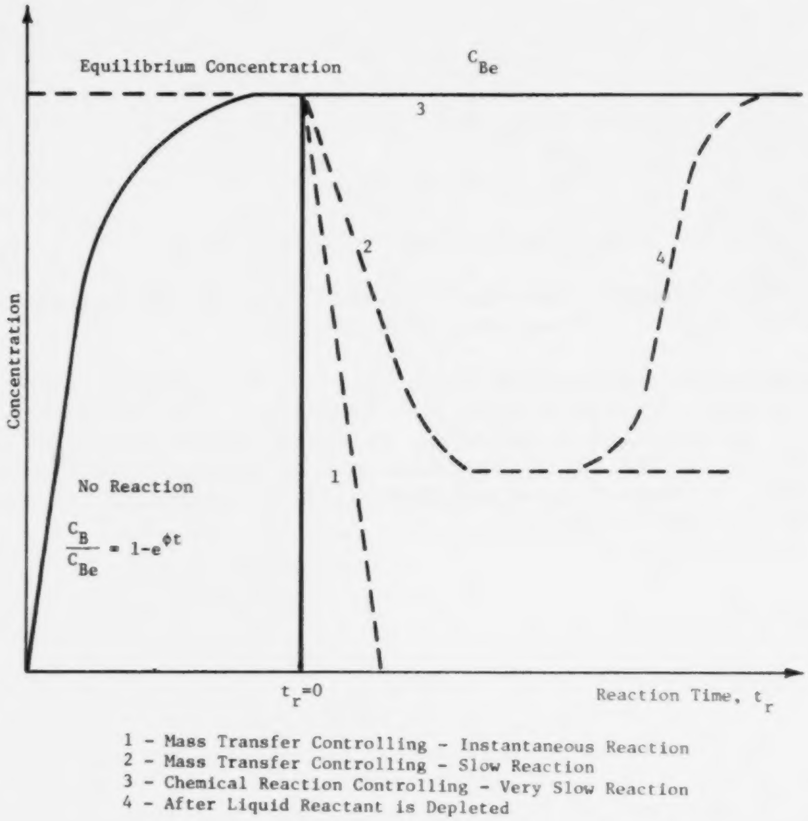
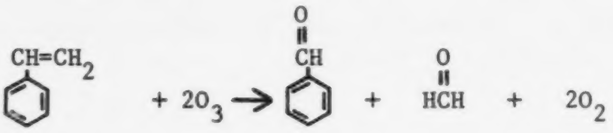
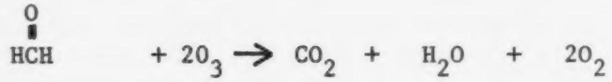


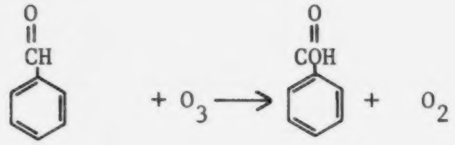
Figure 16. Liquid phase concentration of the gas-phase reactant as presented by the macroscopic view of interphase mass transfer with chemical reaction for semi-batch operation. Probable reaction regimes are illustrated.

Previous studies have shown that ozone oxidizes styrene to benzaldehyde, which is easily oxidized to benzoic acid (6,7). The ozone attack on benzoic acid should be directed to the meta positions, but actually occurs to some extent at all positions, including the carboxylic acid group. The study (5) was simplified by not extending the analytical work beyond benzoic acid in search of the various reaction products. The chemical reactions studied were:

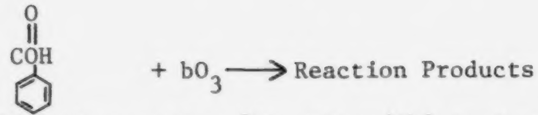

(3)



$$\overset{O}{\overset{\|}{HCH}} + 2O_3 \rightarrow CO_2 + H_2O + 2O_2 \qquad (4)$$



(5)



(6)

The formaldehyde reaction [Reaction (4)] is instantaneous and was incorporated into the initial styrene ozonation reaction.

The successive ozone attack on styrene and its reaction products is similar to certain important industrial reactions, such as the successive substitutive halogenation or nitration of hydrocarbons, and the addition of alkene oxides to proton donor compounds such as amines, alcohols, water, and hydrazine. A general representation of these reactions including the ozonation of styrene is written:

$$A + b_1B \xrightarrow[k_1]{} R \qquad (7)$$

$$R + b_2B \xrightarrow[k_2]{} S \qquad (8)$$

$$S + b_3B \xrightarrow[k_3]{} T \qquad (9)$$

where A is liquid reactant A, B is ozone, b is stoichiometric mole ratio of moles of ozone per mole of liquid reactant, and R, S, T are liquid reactants, and k_1, k_2, k_3 are reaction rate constants. This reaction mechanism is considered to be consecutive with respect to compounds A, R, S, and T and parallel with respect to compound B, ozone.

The rate expressions for the consecutive-parallel reactions, assuming the reactions are irreversible, bimolecular, and of constant density, are

$$\text{Stryene} \qquad r_A = \frac{dC_A}{dt} = -k_1C_AC_B \qquad (10)$$

$$\text{Benzaldehyde} \quad r_R = \frac{dC_R}{dt} = k_1C_AC_B - k_2C_RC_B \qquad (11)$$

$$\text{Benzoic Acid} \quad r_S = \frac{dC_s}{dt} = k_2C_RC_B - k_3C_SC_B \qquad (12)$$

Levenspiel (8) has discussed the consecutive-parallel reaction type and presents a general solution to the rate equations.

Mass Transfer Model

The mass-transfer equations were extended to include the chemical reactions by inserting the rate equations (10), (11), and (12) for the reaction term in equation (1). The following assumptions were made during the development to simplify the equations:

1. Well-mixed semibatch stirred tank reactor operation of continuously sparged gas into a constant volume of liquid.

2. Constant temperature and pressure.

3. Constant volume and liquid density.

4. Constant molar gas feed rate.

5. Constant gas holdup.

6. Ozone decompose via first order reaction.

7. Liquid reactants and products are nonvolatile.

The model was developed for the probable reaction regimes of liquid-phase mass transfer controlling with an instantaneous reaction and a slow reaction either mass transfer controlled or reaction rate controlled. The deciding factor is whether or not ozone penetrates the bulk liquid. If ozone does penetrate the bulk liquid, and if the reaction is extremely slow and ozone reaches an equilibrium concentration in the liquid, the reaction is rate controlled. Both models were applied to the experimental data to determine the controlling regime.

The initial model was developed for mass transfer controlling with an instantaneous reaction for the single reaction given in Equation (7). The liquid reactant A represents the initial reactant which can be styrene, benzaldehyde, or benzoic acid. The ozone does not penetrate into the bulk liquid for a truly mass-transfer limiting system. Thus, the molar balances are simplified. The rate of disappearance of A can be found from the stoichiometry of the reaction and the limiting form of the ozone balance to give a solution in terms of the ozone transferred from the gas phase:

$$\frac{N_A}{N_{Ao}} = 1 - \left(\frac{Gy_{Bb}}{N_{Ao}b_1}\right) t \qquad (13)$$

Deviation of experimental data from the line projected by equation (13) indicates a slow reaction controlling. The mass-transfer limiting line was calculated for each test.

If the ozonation reaction is slow, either mass transfer controlling with a slow reaction or reaction rate controlling, the ozone will penetrate into the bulk liquid. In the latter case, the ozone reaches its equilibrium value as predicted by Henry's law. For the model development, an average ozone bulk concentration, $\bar{x}_B$, was used. Allowing $\bar{x}_B$ to be a constant transforms the reaction into the form of a pseudo first order reaction of which the solution is

$$\frac{N_A}{N_{Ao}} = e^{-\omega_1 t} \qquad (14)$$

where:

$$\omega_1 = \frac{k_1 V \bar{x}_B}{L}$$

L = total moles of liquid.

The model was extended for the second reaction involving the reaction product R. Substituting equation (14) into the rate equation for R and integrating, the solution for the moles of R at any instant is expressed as

$$\frac{N_R}{N_{Ao}} = \frac{\omega_1}{\omega_2 - \omega_1} (e^{-\omega_1 t} - e^{-\omega_2 t}) \qquad (15)$$

These models were applied to the experimental data obtained in the styrene ozonation study.

LABORATORY STUDY

A stirred tank reactor was selected for the ozonation study. The reactor is capable of bringing large quantities of ozone into contact with a specified volume of wastewater. The stirred tank reactor was operated in the semibatch mode, and ozone gas was fed continually to a constant volume of wastewater. The reactor was designed to comply with the standard stirred tank reactor configuration used by Westerterp and others in mass transfer studies (9, 10, 11). Prengle used a similar process for the ozonation of five particular refractory compounds (12). The major dimensions of the reactor are ratioed to the tank diameter for easy design and scaleup. The plexiglass reactor used for this study has a diameter of 39.2 cm and dimensions corresponding to the standard configuration. A volume of approximately 20 liters was achieved with a liquid height of 39.2 cm.

A schematic of the ozone pilot plant is shown in Figure 2. Air was used as a feed gas to the Ozone Research and Equipment Company (OREC) Model 03B4-AR ozonator. The ozonator has a rated capacity of 0.8 kg of ozone per day. The ozone flow to the reactor was controlled by a needle valve. The gas flow was measured with a rotameter, and excess gas was vented through a potassium iodide trap to the atmosphere.

The standard potassium iodide method (13) was used to analyze the ozone concentration in the feed and exit gases and in the liquid. The temperature was monitored periodically. An operational immersion heater and temperature controller were installed to operate at 15° and 25°C.

The gas feed rate was 11.5 l/min, and the feed contained 12-15 mg/l ozone (1.0 to 1.2 wt%). A turbine speed of 700 rpm provided a sufficient volumetric mass-transfer coefficient to consume all of the ozone if the reaction was instantaneous (5). The average test was continued for 3 hr. Liquid samples were analyzed for total organic carbon with a Beckman 915 TOC analyzer and for composition with a gas chromatograph.

MASS-TRANSFER STUDY

Mass transfer of ozone into distilled water and pulse tests were used to study the model reliability and mixing characteristics of the reactor. A standard stirred tank reactor configuration was chosen to approach ideal backmix flow. Deviation from the ideal was determined by pulse testing as described by Levenspiel (8). Standard operating conditions were used during the reaction study; turbine speed was 700 rpm and gas-feed rate was 0.01 m^3/min. A liquid feed rate of 0.003 m^3/min gave a residence time of 8.17 min. Sodium chloride solution was used as a tracer; chloride ion concentration in the exit stream was measured for use in a C curve distribution test.

The C curve described the concentration-time function of the tracer in the exit stream of the reactor in response to an idealized pulse tracer injection. The experimental data for the pulse test, shown as the dotted line in Figure 17, were compared to that plotted in the solid line representing idealized backmix flow in a stirred tank reactor. The experimental data approach the ideal with less than 5 percent error. Though real reactors are never ideal, the reactor used was considered ideal with negligible error.

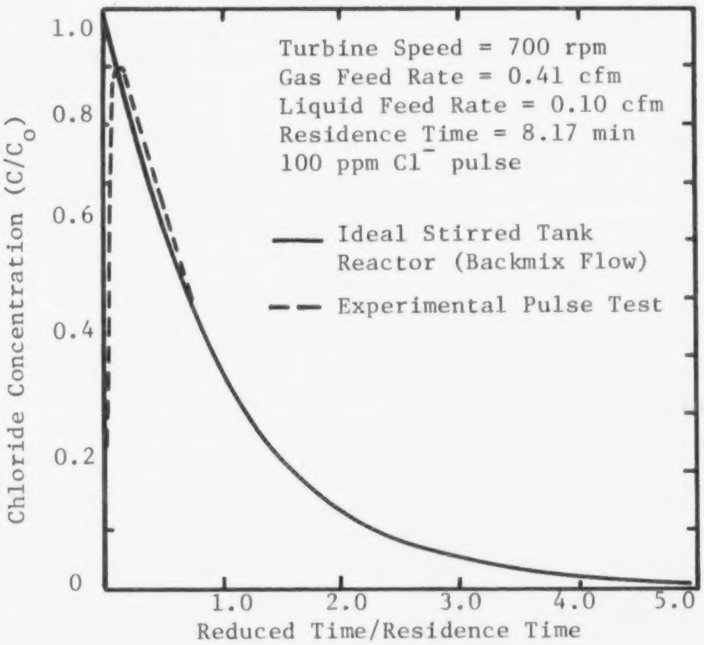


Figure 17. Comparison of ideal and experimental C-curves for a pulse tracer input for a stirred tank reactor.

The effects of temperature, power input, and gas velocity on the volumetric mass-transfer coefficient were evaluated. A total of 83 mass-transfer tests were conducted with various temperatures, turbine speeds, and gas feed rates. The tests were made with the water either chilled between 12° and 15°C or at ambient temperatures of 22° to 25°C. The following turbine speeds were studied: 0, 300, 400, 500, 700, and 900 rpm. These values were transformed into power inputs of 0, 0.18, 0.40, 0.87, 2,4, and 5.3 hp per 1000 liters, respectively. The gas feed rates were varied between 0.004, 0.006, 0.008, and 0.011 m^3/min.

The mass-transfer data were evaluated by plotting the ozone concentration profiles obtained for the various operating parameters. Figure 18 is a plot of the ozone concentration profile for the various turbine speeds at a constant gas feed rate of 0.01 m^3/min and a temperature range of 12° to 15°C. The data showed that the ozone concentration in the liquid increased exponentially to the solubility limit.

A constant gas concentration was not maintained for the mass-transfer studies, giving different equilibrium values for ozone in the liquid for the various tests. For example, test 14 was performed with an ozone gas concentration of 1.24 wt percent, giving an equilibrium value of 6.96 mg/l. Test 3 had a gas concentration of 1.10 wt percent ozone and a corresponding equilibrium value of 5.75 mg/l. The relative differences are shown in Figure 18.

The data in Figure 18 show that the ozone absorption rate into the water was slow without agitation and increased as agitation was applied. The increase in the ozone absorption line slope with the increased turbine speed was a result of shearing the gas bubbles by the turbine blades, thereby increasing the interfacial area. The slopes of the absorption lines above a turbine speed 400 rpm are similar, indicating the system was operating in the well-mixed region between 400 and 900 rpm.

A similar set of figures was generated for the various turbine speeds at constant gas feed rates for the temperature range of 22° to 25°C. Figure 19 is for a gas feed rate of 0.01 m^3/min and is typical of data obtained at other feed rates. The ozone concentration profiles in Figure 19 are almost duplicates of those in Figure 18, except the ozone equilibrium concentration was lower at the higher operating temperatures. Again, the equilibrium concentration levels were dependent on the ozone gas concentrations. The well-mixed region was achieved above a turbine speed of 400 rpm. Careful evaluation of the mass-transfer data showed the small increase in temperature did not significantly change the volumetric mass-transfer coefficient. The data were replotted for the various gas feed rates, holding the turbine speed constant to evaluate the effect of gas feed rate on the ozone mass transfer. Figure 20 is for a turbine speed of 700 rpm and a temperature range of 12° to 15°C. The absorption rate of ozone increased as the gas feed rate was increased.

The volumetric mass-transfer coefficient, $k_L a$, was calculated using the slope of the absorption lines and the relationship.

$$k_L a = \frac{C_1}{\eta - \beta C_1} \left(\frac{L}{v}\right) \qquad (16)$$

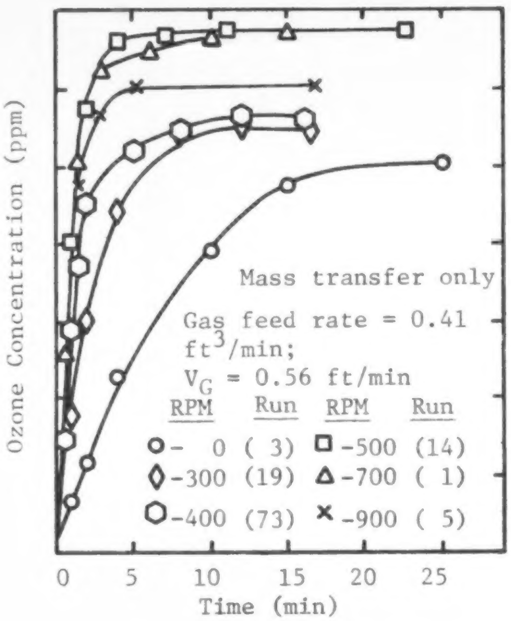


Figure 18. Ozone concentration profile for various turbine speeds at 12°-15°C.

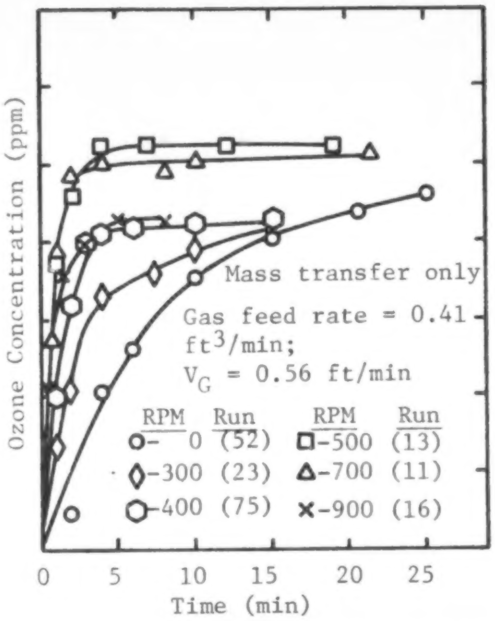


Figure 19. Ozone concentration profile for various turbine speeds at 22°-25°C.

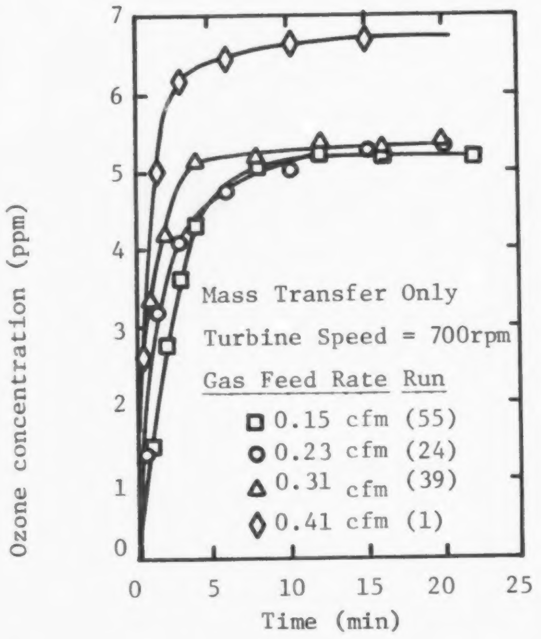


Figure 20. Ozone concentration profile for various gas feed rates at 12°-15°C.

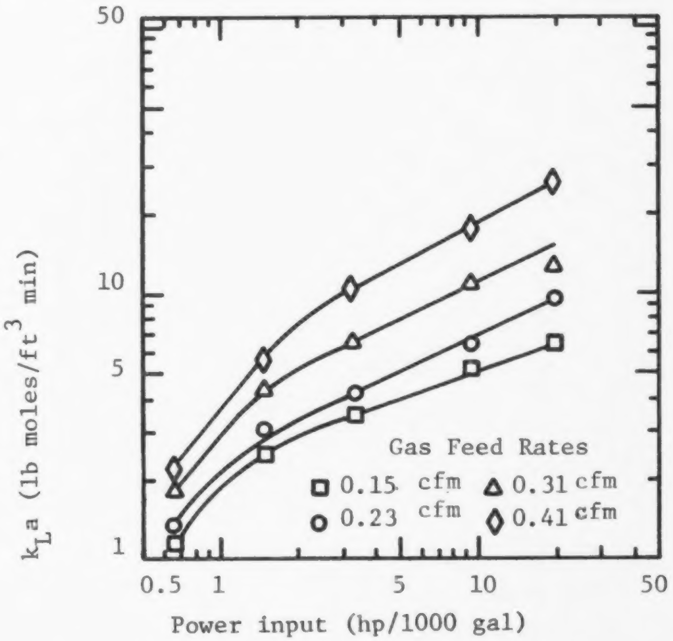


Figure 21. Volumetric mass-transfer coefficient at various gas feed rates as a function of power input.

Correlations were made between the volumetric mass-transfer coefficient, the power input from the turbine, and the gas feed rate. The volumetric mass-transfer coefficient was plotted on log-log paper as a function of the power input with the various gas feed rates as parameters (Fig. 21) and shows the rapid increase in k_La as agitation was applied to the system. A slower increase was achieved in the well-mixed region. This figure is similar to that published by Oldshue (15) for oxygen transfer into active milk sludge. The slope of Oldshue's data in the well-mixed region was 0.48, while the slopes in Figure 20 varied from 0.31 to 0.49, with an average value of 0.43. Kawecki (10) reported similar curves for the volumetric mass-transfer coefficient and power input.

Cooper, et al. (9) investigated the absorption of oxygen from air into aqueous sodium sulfite solutions. Cooper found the following correlations between the mass-transfer coefficient and the power input and superficial gas velocity.

$$k_La = m_1 \; V_G^{0.67} \tag{17}$$

$$k_La = m_2 \; (P/V)^{0.5} \tag{18}$$

Cooper's equations suggest a log-log plot of $k_La/V_G^{0.67}$ versus (P/V) would give a straight line with a slope of 0.5. The mass-transfer data were plotted in such a manner in Figure 22 to produce a curve similar to Cooper's. The slope of the line was 1.15 in the lower power input region and 0.46 in the well-mixed region. (Cooper reported a maximum slope of 0.98 in his data). The correlation given by eq. (17) was tested by plotting volumetric mass-transfer coefficient as a function of the superficial gas velocity with the turbine speed as a parameter on log-log paper. In the absence of agitation, a straight-line relationship with a slope of 0.66 was obtained (Fig. 23). The data show a similar slope at lower superficial gas velocities, but a rapid increase as the superficial gas velocity and power input were intensified. The slope varied from 0.98 to 2.10. Yashida (18) found his mass-transfer data to correlate well with superficial gas velocity raised to the 0.74 power. Both Cooper and Yashida studied lower superficial gas velocities than used in the tests. Foust (19) reported a slope of 2.13 for a superficial gas velocity range of 0.3 to 1.5 m/min and similar power inputs. The various correlations reported between the volumetric mass-transfer corfficient and the superficial gas velocity proves there is a transition range where the exponent varies significantly. Both Calderbank (20) and Fair (21) report a transitional range in the volumetric mass-transfer coefficient using bubble diameter instead of superficial gas velocity as a parameter.

The volumetric mass-transfer coefficient was evaluated by Majumoar (26) in a bubble column to be 16.18 Kg mole/m^3 min. A value of 9.6 Kg mole/m^3 min was found under similar operating conditions using Figure 23. The fact that Majumoar's mass-transfer model did not include a reaction term for the decomposition of ozone explains the slight deviation between the two values. The excellent correlation between mass-transfer data obtained using this model and published data supports the accuracy of the mass-transfer data and the model developed.

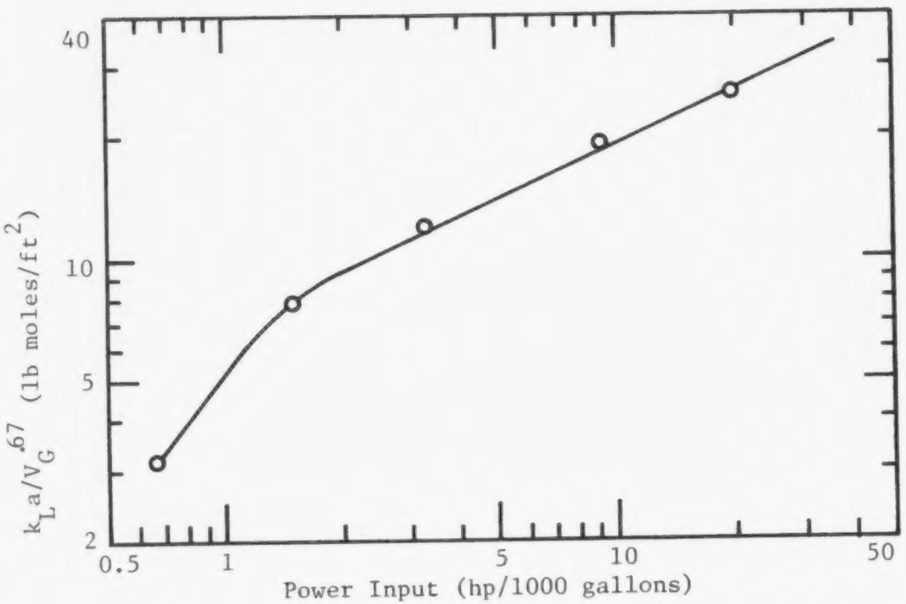


Figure 22. Volumetric mass transfer coefficient corrected for superficial gas velocity as a function of power input.

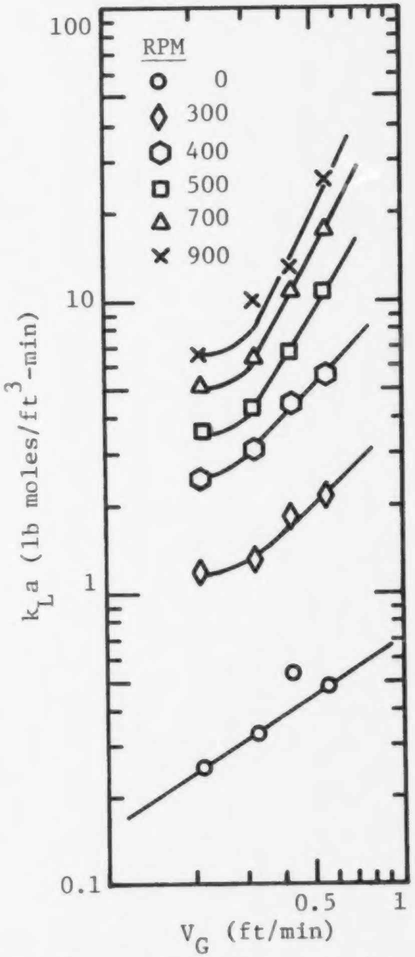


Figure 23. Volumetric mass transfer coefficient at various turbine speeds as a function of superficial gas velocity.

PILOT STUDIES

An ozone pilot plant was designed and constructed for the project. It was housed in a portable 2.4 x 3 m building with a major equipment arranged as shown in Figure 24. The pilot unit was equipped with titrimetric apparatus for the determination of ozone concentration in the gas and liquid phases.

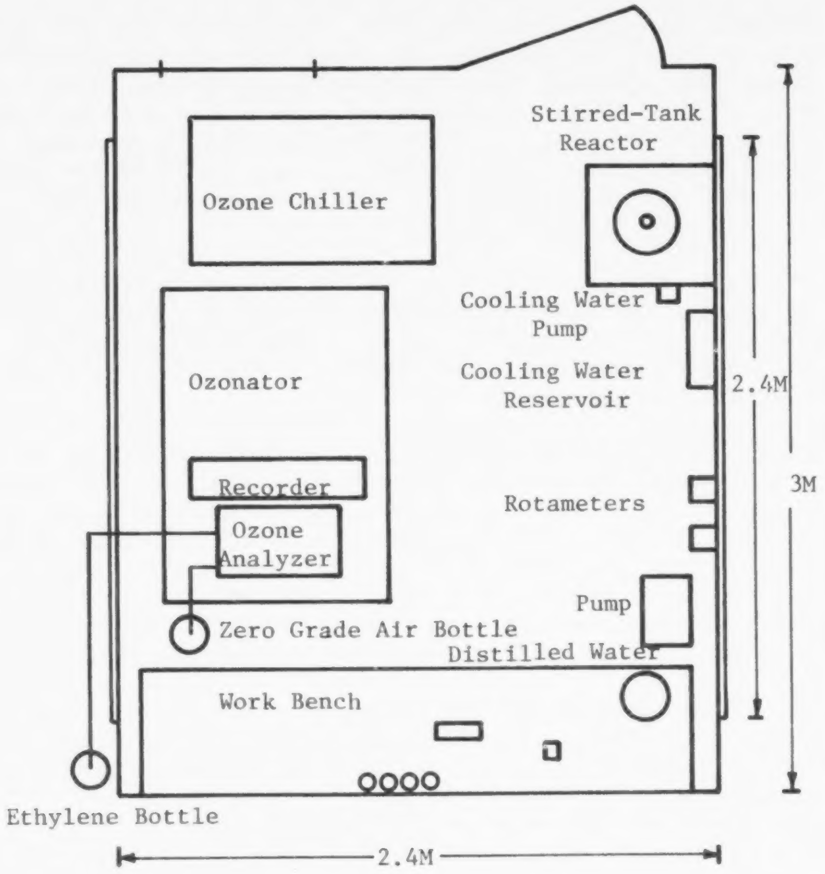

Stirred-Tank Reactor
Ozone Chiller
Cooling Water Pump
Ozonator
Cooling Water Reservoir
2.4M
3M
Recorder
Rotameters
Ozone Analyzer
Pump
Zero Grade Air Bottle
Distilled Water
Work Bench
Ethylene Bottle
2.4M

Figure 24. Equipment arrangement in ozone pilot plant building.

Ozone is a toxic gas with a threshold limit value (TLV) of 0.1 mg/l. Masks equipped with activated charcoal filters were used for protection. Draeger tubes were used to detect ozone concentrations in the work area, while a Beckman continuous ozone analyzer monitored ozone levels in the pilot plant building. The analyzer concentration range was 0.1 to 10 mg/l ozone in air. The sensitivity of the Draeger tubes was 0.05 to 300 mg/l. Explosion-proof electrical outlets and switch boxes were used. The building was designed with two 120 x 240 cm flaps and a fan to promote ventilation through the building.

Equipment

An Ozone Research and Equipment Company (OREC) model 0384-AR ozone generator was used to produce ozone. The ozonator contained five dielectrics and had a rated capacity of 1 kg of ozone per day. The ozonator included an air compressor and a chiller.

Reactor Systems--

A tubular reactor was constructed to simulate pipeline flow and provide an easy adaptation to plant use (Fig. 25). The reactor was made of 18 mm polypropylene tubing. The ozone gas and wastewater were dispersed with a nozzle or mixed in a standard tee, with gas-liquid contact being induced by static mixers. A Masterflex variable speed pump was used to vary the wastewater flow rate from 1 to 4 liters/min. Rotameters were used to measure gas and liquid flow rates; excess gas was vented to the atmosphere. Sample valves were placed at the reactor midpoint and at the end of the 70-m reactor.

The tubular reactor was used only on the toluene diisocyanate wastestream. Analysis of the reaction mechanism showed that 0.5 m^3 of 1.5 wt percent ozone gas would be needed to treat 4 liters of wastewater. The volume of air introduced with the ozone makes a tubular reactor impractical except for low TOC wastestreams.

A schematic of the stirred tank reactor system, including the ozone generator and distributing network is shown in Figure 26. The reactor was operated in the semibatch mode to contact large quantities of ozone to a specified volume of water. The reactor could easily be converted to a continuous system with the addition of a liquid feed pump. The reactor was designed to comply with the standard stirred tank reactor configuration used by Westerterp and others in mass-transfer studies (9-11). Prengle used a similar process for several ozonation studies (12, 23, 25).

The major dimensions of the reactor were ratioed to the tank diameter for easy design and scaleup. The Plexiglas reactor had a diameter of 30 cm and dimensions corresponding to the standard configuration shown in Figure 27. A liquid volume of 20 liters was achieved with the proper ratioed liquid height of 30 cm. The reactor was well insulated and wrapped with cooling coils to maintain a constant temperature.

A rotameter was used to measure the gas flow to the reactor. Needle valves were used to control the gas flow, with excess gas vented to the atmosphere through a potassium iodide trap to deplete the ozone. Gas sample ports were located on the ozonator and on the gas exit line from the reactor. Liquid samples were withdrawn from either the side liquid sample points or through the bottom sample port.

An optional immersion heater and temperature controller were available for operating at temperatures between 24° and 121°C. Actual tests were conducted at 15° and 25°C utilizing ice water circulating through cooling coils to maintain an isothermal operation. Bayonette thermometers were used to measure operating temperatures. Various degrees of mixing were achieved with the variable speed mixer.

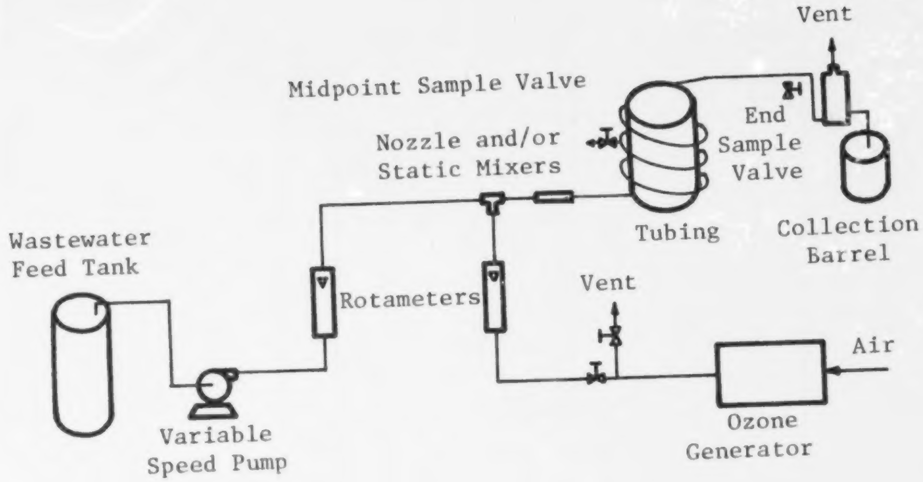

Vent
Midpoint Sample Valve
Nozzle and/or
Static Mixers
End
Sample
Valve
Tubing
Collection
Barrel
Wastewater
Feed Tank
Rotameters
Vent
Air
Variable
Speed Pump
Ozone
Generator

Figure 25. Tubular reactor schematic.

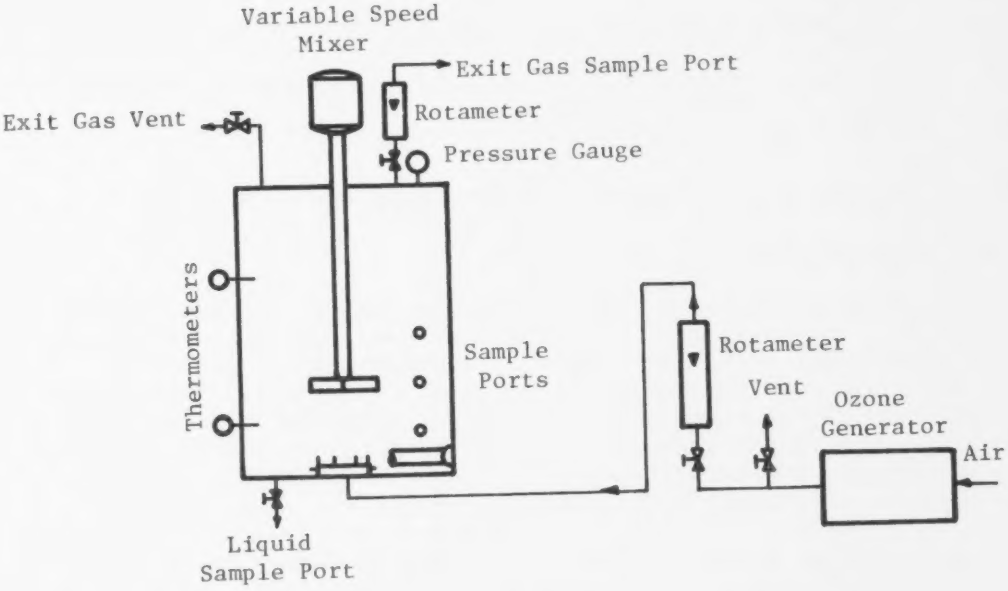
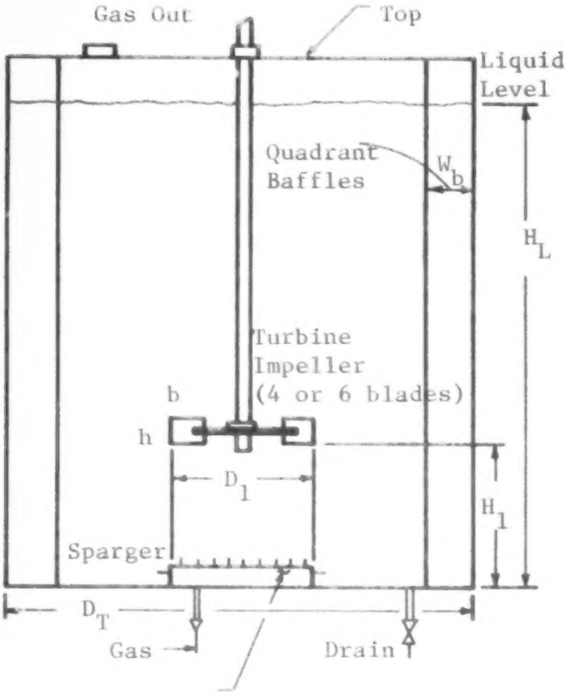

Variable Speed
Mixer
Exit Gas Sample Port
Exit Gas Vent
Rotameter
Pressure Gauge
Thermometers
Sample
Ports
Rotameter
Vent
Ozone
Generator
Air
Liquid
Sample Port

Figure 26. Ozone pilot plant schematic.



Dimensions: $H_L = D_T$, $W_b = D_T/3, H_1 = D_1$

Sparger Holds: 3-1/16" holes/in^2 of sparger cross-section

Impellers: $b = D_1/4$, $h = D_1/5$

Figure 27. Standard reactor configuration.

Experimental Procedures

A gas chromatograph was used to analyze the styrene and benzaldehyde concentrations. The benzoic acid concentration was measured by monitoring the ultraviolet light absorption with a spectrophotometer. The total organic carbon was used to monitor the reaction of the industrial process wastestreams and was measured with a Beckman TOC analyzer. The standard potassium iodide method was used to analyze the ozone concentration in the gas and was adjusted to analyze ozone concentration in the liquid. The turbine speed was monitored with a phototachometer.

After ozonation, biological batch tests were performed to determine the enhancement of ozonation on wastewater biodegradability. An acclimated seed was added to each of the test reactors. Various amounts of wastestream were added to the test reactors to obtain a series of organic loadings. One reactor containing only acclimated seed was used as a baseline. Data were collected on the reactors during a 3-day test period.

The tests were conducted in two separate phases. First, mass-transfer data were collected on ozone transferring into the distilled water. The second phase was the gas-liquid reaction study. Toluene diisocyanate wastewater was studied initially, followed by the the other industrial wastes. Benzoic acid was the first organic ozonated in aqueous solution followed by benzaldehyde and styrene. The individual reactions were studied to evaluate the rate constants for the continuous-parallel reaction system.

Mass-transfer tests were conducted with ozone transferring into distilled water. The water was placed in the reactor to give a height-to-diameter ratio of one. The desired operating temperature was obtained before setting the turbine speed. Once the turbine speed was established, ozone was introduced into the bottom of the reactor through the gas sparger. Final adjustments were made to obtain the desired gas feed rate. The reactor was operated isothermally during the test and was sampled and analyzed routinely for ozone content.

The reaction procedure began with the preparation of 20 liters of test solution with the desired concentration of liquid reactant. The solution was introduced into the reactor and the pH and temperature were adjusted. Concentrated sulfuric acid and a sodium hydroxide-sodium carbonate buffering solution were used to adjust the pH to values of 2 and 11, respectively. After establishing a turbine speed of 700 rpm, an initial baseline liquid sample was taken. The reaction was initiated with the addition of ozone gas. Final adjustments were made to obtain the desired gas feed rate. Ozone analyses were performed on the liquid and the feed and exit gases during the test. Liquid samples were taken at pre-determined intervals through either the side or bottom sample port. Temperature and pH were recorded with each liquid sample which was sealed in an air-tight sample vial.

The standard operating parameters chosen for the reaction tests were a gas feed rate of 11.5 liters/min containing 12-15 mg/liter ozone (1.0 to 1.2 wt%). A turbine speed of 700 rpm provided a sufficient volumetric mass-transfer coefficient to consume all the ozone for a mass-transfer controlling regime with an instantaneous reaction. The tests were conducted isothermally for 150 min.

Ozonation Reaction Study--

The wastewaters studied were taken from the four processes listed in Table 93. The streams were not analyzed for individual components, but were characterized for the significant properties listed in Table 94. The wastewaters were ozonated at their normal TOC concentrations as received and after dilution to 100 to 150 mg/l TOC. The dilution tests were performed to reduce the ozonation time. The ozone studies were conducted with a gas feed rate of 11.5 liters/min and a turbine speed of 700 rpm. The ozone transferred into the water and reacted with the organics was calculated from a material balance across the reactor. The data obtained in the study were plotted as the function TOC remaining (TOC/TOC_o) versus time and weight ratio of milligrams ozone transferred (reacted) per milligram TOC. Extrapolation of the weight ratio line to zero TOC remaining gave the weight of ozone required for complete oxidation. This was used to determine if the reaction was mass-transfer limited. Deviation from the mass-transfer limiting line indicated the reaction was reaction-rate controlled.

TABLE 93. PROCESS WASTESTREAMS USED FOR THE OZONATION STUDY WITH THEIR RANGE OF TOC CONCENTRATIONS FOUND

Major Contaminant	TOC Range (mg/liter)
Toluene Diisocyanate - TDI	250-3500
Ethylene Glycol - Polyol	150-1500
Styrene	30-200
Ethylene Dichloride - EDC (Steam Stripped)	300-1500

TDI Wastewater--

The first wastewater ozonated was a wash stream from a toluene diisocyanate (TDI) process. In the process, phosgene was reacted with toluene diamine (TD) to product TDI, which is used in the manufacture of polyurethane. The TDI wastewater characterization is given in Table 94. The water is believed to be contaminated with toluene, amines, and TDA.

The tubular reactor system was tested with the toluene diisocyanate wastewater. Complete dispersion of the gas and liquid was achieved with a nozzle, but at a liquid feed rate above 2 liters/min, the nozzle forced liquid into the ozone gas supply line due to high pack back pressure. The ozone generator was operated at 1.3 atm pressure compared to the optimum of 1.02 atm to force ozone into the liquid. The gas and liquid separated into distinct layers 1.5 m downstream of the nozzle. The gas-liquid flow configuration was accurately predicted by the Baker and Govier charts, which describe gas-liquid flow in horizontal and verticle pipes.

TABLE 94. CHARACTERIZATION OF INDUSTRIAL WASTEWATERS OZONATED (Averaged Data; Concentrations in mg/liter)

Compound	TDI	Polyol	Styrene	EDC
pH	11.6	11.4	11.8	1.3
TOC	687	476	85	866
COD	663	1509	225	1309
TOD	439	1065	227	1940
Phenol	6.6	--	1.9	--
Cl$^-$	2500	70	3100	6800
Acidity*	--	--	--	8233
Alkalinity*	2408	240	2733	--
Suspended Solids	11.83	4.80	3.85	7.97
Volatile Suspended Solids	3.07	1.40	1.04	0.86
Residual Chlorine	--	--	--	65.25

* Measured as $CaCO_3$ with phenolphthalein end point.

The residence time in the tubular reactor was controlled by the gas flow and was recorded by visual timing of the liquid through the reactor. A constant liquid feed rate of 2 liters/min was chosen, and the gas feed rate was changed to vary residence times. Samples were taken at both the midpoint and end sample point to give two residence times per run. All samples were collected after steady-state operation was achieved. The feed gas and exit gas were sampled routinely for ozone concentration. On a majority of the runs, ozone was not detected in the exit gas. A summary of the ozonation runs with the nozzle is given in Table 95. The mole ratio was calculated on the basis of the TOC being pure TDA. Since the data are fairly scattered, the area available for mass-transfer is reduced.

TABLE 95. OZONATION OF TOLUENE DIISOCYANATE WASTEWATER IN A TUBULAR REACTOR WITH NOZZLE DISPERSION

Liquid Flow = 1.75 l/min Original TOC = 560 mg/l

Gas Flow (l/min)	Residence Time (min)	TOC (mg/l)	Reduction (%)	Mole Ratio
pH = 11				
3.5	1.8	586	0	0.059
3.5	3.7	561	0	0.059
6.0	1.3	528	5.7	0.102
6.0	2.6	549	2.0	0.102
8	1.0	520	6.2	0.127
8	2.0	512	8.6	0.127
pH = 8				
4	1.7	891	12.3	0.064
4	3.4	544	2.9	0.064
8	1.0	491	12.3	0.127
8	2.0	481	14.1	0.127
pH = 1				
4	1.7	538	4.0	0.068
4	3.4	530	5.4	0.068
8	1.0	527	5.9	0.135
8	2.0	541	2.0	0.135
pH = 6				
8	1.0	663	0	0.135
8	2.0	538	5.0	0.135

Static mixers were added to promote gas-liquid contact. The pressure drop was greatly reduced with the static mixers and worked well in their immediate area. A liquid flow rate of 1.5 l/min was used, with higher gas flows used to increase the ozone to TDA mole ratio. Table 96 lists the TOC reductions for the tubular reactor runs using the static mixers. The TOC reductions were low, with the largest value being 15%. The tubular reactor system was abandoned because of the inefficiency of mixing the gas and the liquid.

TABLE 96. OZONATION OF TOLUENE DIISOCYANATE WASTEWATER IN A TUBULAR REACTOR WITH STATIC MIXERS

Liquid Flow = 1.5 l/min Original TOC = 1068 mg/l

Gas Flow (l/min)	Residence Time (min)	TOC (mg/l)	Reduction (%)	Mole Ratio
pH = 1				
10	1.5	970	9.2	0.176
10	3.0	938	12.2	0.176
24	1.0	965	9.6	0.424
24	2.0	933	12.6	0.424
26	0.7	965	9.6	0.451
26	1.4	965	9.6	0.459
pH = 8				
10	1.5	1118	0	0.220
10	3.0	1046	2.1	0.200
20	0.8	946	9.7	0.396
20	1.6	1026	3.9	0.396

BOD_5 to TOC Ratios

Sample	BOD_5 (mg/l)	TOC (mg/l)	Ratio
Unreacted TDI	1161	1068	1.087
0.200 moles O_3/mole TDI	1341	1048	1.239
0.396 moles O_3/mole TDI	1251	964	1.257

The stirred tank reactor was then used to study the ozonation reactions. The effects of pH, temperature, and ferrous sulfate catalyst were studied and are shown in Figure 28. The curvature in the TOC line is a result of the reaction of TDA and amines. Ozone will oxidize an amine group to the nitro group without a TOC decrease since no organic carbon is released. BOD_5 and biological batch tests were performed because nitro groups are easier to biodegrade than amines. Extrapolation of the plots indicates a weight ratio of 7 mg O_3/mg TOC will completely oxidize the organic compounds. The dark red TDI waste was decolorized to a faint yellow at a weight ratio of two. The maximum TOC reduction achieved after 3 hr of ozonation was 26 percent. Figures 28 and 29 show that variation in pH, temperature, and catalyst addition did not alter the reaction significantly. Tests with ferrous sulfate catalyst were performed in acidic solutions to prevent precipitation of the iron.

A concentrated waste sample (TOC = 3360 mg/l) was ozonated for 6 hr before being submitted to biological batch tests. The TOC reduction was 15.6 percent. The organic loadings and summary data from the batch tests for the raw TDI and ozonated TDI stream are listed in Table 97. Each reactor was analyzed periodically for TOC, oxygen utilization rate, BOD_5 and MLVSS over

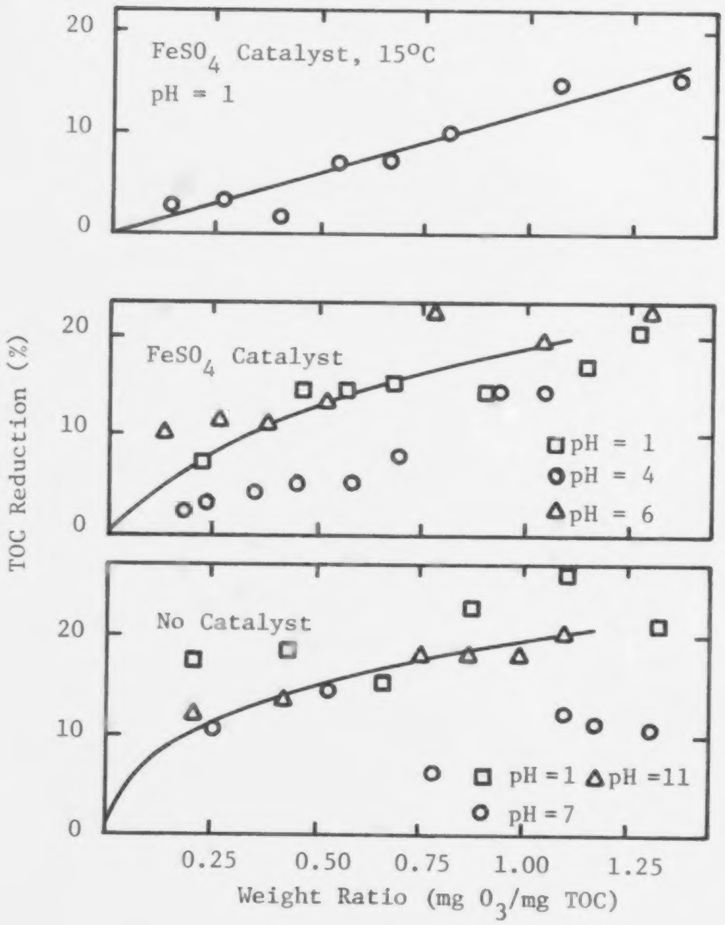


Figure 28. Ozonation of toluene diisocyanate wastewater as a function of ozone transferred

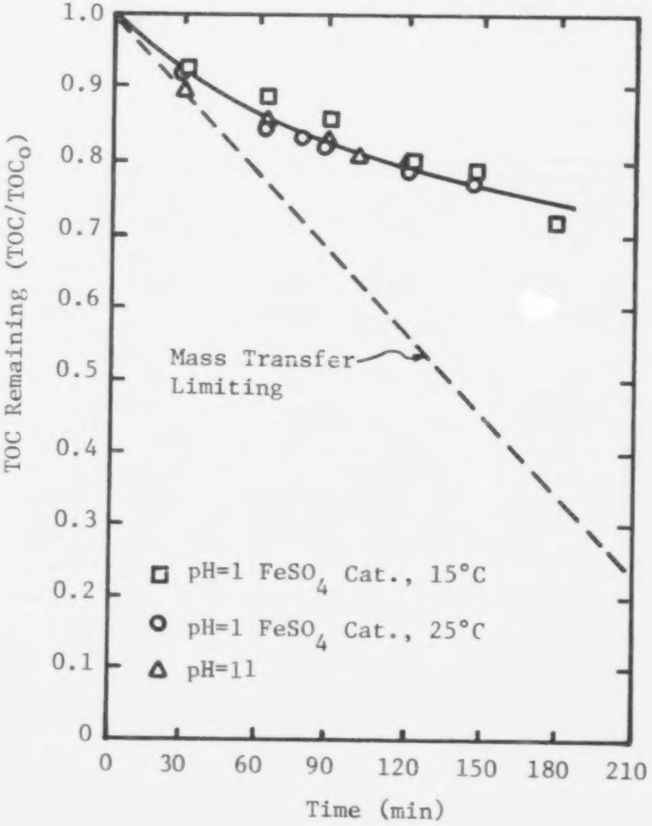


Figure 29. Ozonation of toluene diisocyanate as a function of time.

TABLE 97. SUMMARY OF BATCH STUDY RESULTS FOR RAW AND OZONATED TDI WASTEWATER

	Reactor 1		Reactor 2		Reactor 3		Reactor 4		Reactor 5	
Time (hours)	0	24	0	24	0	24	0	24	0	24
Untreated TDI										
F/M	0.05		0.10		0.20		0.40		Airstripped	
TOC (mg/l)	243	238	370	347	652	621	1221	1118	1136	1315
TOC (% Reduction)		2.1		6.2		4.6		8.4		1.6
BOD_5 (mg/l)	46	48*	50	26*	69	64*	83	48*	109	75*
BOD_5 (% Reduction)		0	48.0		0		42.2		31.2	
Ozonated TDI										
F/M	0.05		0.10		0.20		0.40		Airstripped	
TOC (mg/l)	183	149	274	239	512	445	1035	962	1003	1097
TOC (% Reduction)		18.6		12.8		19.1		7.1		0
BOD_5 (mg/l)	39	60*	125	34*	215	120*	306	86*	465	286*
BOD_5 (% Reduction)		0		72.8		44.2		71.9		38.5

*Reading taken at 72 hr.

a 3-day period. The BOD_5 for the ozonated waste was reduced 30 percent more than that for the untreated waste. The reductions were associated for F/M ratios of 0.1 and 0.4. TOC reductions were also up to 4 times greater for the ozonated waste.

Polyol Wastewater--

The polyol wastewater was taken from an ethylene glycol process plant. The water was very basic (pH = 11.4) with a grayish tint. It was believed to contain ethylene glycol and other hydroxy hydrocarbons. Ozonation data plotted in Figure 30 show a weight ratio of 7.3 mg of ozone would be required per mg of TOC for complete oxidation as compared to 10 mg for pure ethylene glycol. The effect of pH is dramatically shown in Figure 31, as the TOC reduction is negligible with low pH solutions. The polyol waste oxidation is very pH dependent as is the phenol oxidation with ozone (24). The oxidation proceeded slightly faster with a low operating temperature (15°C) but in both cases the system is controlled by the reaction. The tapering effect is a result of the formation of a refractory compound such as acetic. The ozone concentration reached equilibrium after 150 min.

A batch study was performed on polyol waste which had an initial TOC of 830 mg/liter. After 5 1/2 hr of ozonation, the TOC batch study consisted of 3 test reactors at organic loadings of 0.05, 0.10, and 0.15 mg BOD_5 per mg MLVSS-day. A reactor to test air stripping and a baseline reactor containing only microbial seed were included. Table 98 is a summary of the test results. The raw polyol wastestream was resistant to biological degradation; only 7 to 23 percent of the TOC was removed, yielding residual levels of 142-301 mg/l TOC. The initial BOD_5 levels were low (16 to 28 mg/l) and showed no reduction during the study.

Pretreatment of the polyol wastewater with ozone had a dramatic effect on the degradability of the waste. As seen in Table 98, 45 to 68 percent of the TOC and 83 to 89 percent of the BOD_5 were removed in 72 hr. Ozonation formed volatile organics, as 58 and 72 percent reductions in TOC and BOD_5 were achieved with air stripping, respectively.

The polyol oxidation with ozone is pH dependent and proceeds faster at a pH above 10. A quick TOC reduction is achieved until a refractory compound is produced to slow the reaction rate. The average TOC reduction within 3 hr of ozonation was 50 percent for an initial TOC of 100 mg/l. The effectiveness of ozonation is clearly illustrated in Table 99; the TOC reduction after 5-1/2 hr was only 25 percent but the BOD_5 was increased from 91.3 to 613.5 mg/l (671 percent). The ozonation improved the wastewater biodegradability and could effectively be used as a pretreatment to biooxidation. However, the resistance of the refractory compound would decrease the feasibility of using ozone for complete oxidation.

TABLE 99. COMPARISON OF RAW AND OZONATED POLYOL WASTEWATER

	TOC (mg/l)	BOD_5 (mg/l)	BOD_5/TOC
Raw	830	93.1	0.11
Ozonated	626	613.5	0.98

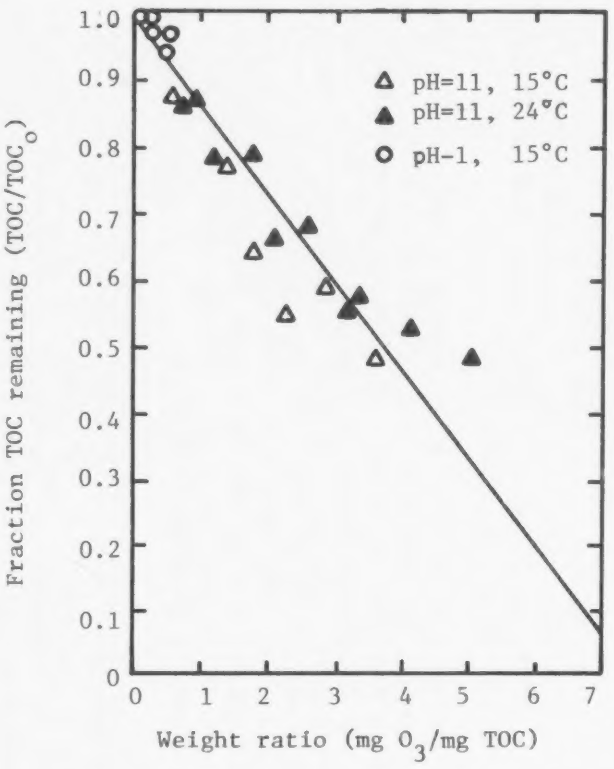


Figure 30. Ozonation of polyol wastewater as a function of ozone transferred

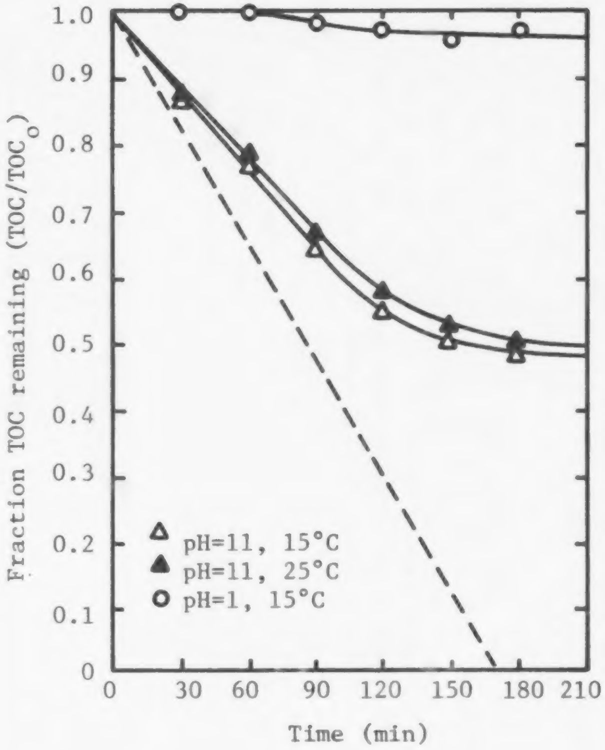


Figure 31. Ozonation of polyol wastewater as a function of time.

TABLE 98. SUMMARY OF BATCH STUDY RESULTS FOR RAW AND OZONATED POLYOL WASTEWATER

	Reactor 1		Reactor 2		Reactor 3		Reactor 4		Reactor 5	
Time (hours)	0	72	0	72	0	72	0	72	0	72
Untreated TDI										
F/M	0.05		0.10		0.15		Airstripped		--(Baseline)	
TOC (mg/l)	162	142	285	264	390	301	385	398	38	54
TOC (% Reduction)		12		7		23		0		0
BOD_5 (mg/l)	16	20	11	28	11	31	51	31	16	22
BOD_5 (% Reduction)		0		0		0		39		0
Ozonated TDI										
F/M	0.05		0.10		0.15		Airstripped		(Baseline)	
TOC (mg/l)	238	130	354	116	404	130	363	151	160	135
TOC (% Reduction)		45		67		68		58		16
BOD_5 (mg/l)	138	23	303	32	395	60	485	120	27	20
BOD_5 (% Reduction)		83		89		87		75		26

Styrene Wastewater--

Styrene is an important chemical in the production of plastics and synthetic rubber. The monomer is usually produced by the dehydrogenation of ethylbenzene. In the process there are two wastewater streams which are combined in the plant effluent. The styrene wastewater had the lowest TOC of the 4 waste streams sudied with an average value of 90 mg/l.

Figure 32, the weight-ratio plot, shows that all the oxidation tests produced sharp decreases in TOC and then leveled off. This was a result of the air stripping of the organics such as styrene from the water. The high pH tests show a TOC reduction after air stripping; by contrast, tests with acidic solutions show a horizontal reduction line. Extrapolation of the basic data showed a weight ratio of 12.5 is required for complete oxidation of the remaining organics as compared to theoretical values of 10 and 10.5 for styrene and ethylbenzene, respectively.

Figure 33 illustrates the effectiveness of air stripping. The air stripped test produced a quicker TOC reduction than the ozonated tests. The lower air stripping values are accounted for by the volatile reactants that are oxidized to a soluble product which reenters the liquid phase. Residual organics were biodegradable, and therefore, batch tests were not performed on the ozonated waste. Continuous biotreatment tests were made at both the laboratory and pilot plant levels. The TOC and BOD_5 reductions were significant in both tests and indicated that ozone could be used as a final oxidation step after biotreatment.

EDC Wastewater--

The last wastestream studied was from an ethylene dichloride process. The water-white stream was very acidic and had a high chloride and residual chlorine content. The stream was highly biorefractory and contained EDC and other volatiles. These were easily steam stripped from the wastewater to reduce the average TOC from 1000 to 400 mg/l. The overhead stream from the stipper was primarily EDC and could be recycled to the process. The bottom stream from the steam stripper was ozonated and studied for biotreatability. The stripped EDC stream reacted well with ozone after adjustment to a basic pH. An 82 percent TOC reduction was achieved within 3 hr of ozonation. Figure 34 indicates a weight ratio of 5.6 mg O_3/mg of TOC is required for complete oxidation. Pure EDC would require a ratio of 12. The initial dip in the TOC fraction is due to air stripping. Air stripping and ozonation were less effective at low pH values, as shown in Figures 34 and 35. The actual TOC reduction fell below the mass-transfer limiting line in Figure 35 due to air stripping. The reaction is fairly rapid and the reaction regime approaches that of a mass-transfer limiting regime. The EDC wastewater with a pH above 10 had the highest ozone utilization of those studied. It is possible that the reaction could be carried to complete oxidation for this waste stream.

Biological batch tests were performed on both stripped and ozonated stripped EDC wastewater. Preliminary batch tests on stripped EDC wastewater which was ozonated for 3 hr showed the TOC was reduced below a minimum to produce significant results. Therefore, a sample was ozonated for 30 min to maintain a treatable TOC level. The TOC was reduced from 409 to 286

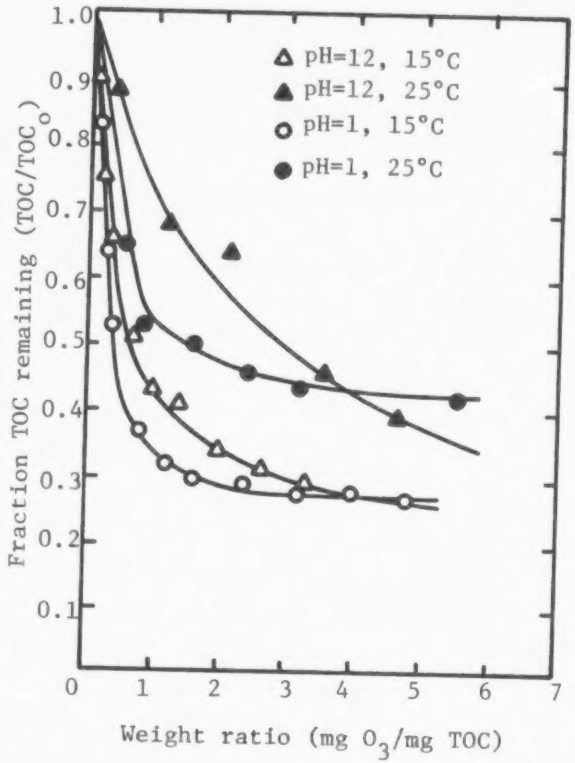


Figure 32. Ozonation of styrene wastewater as a function of ozone transferred.

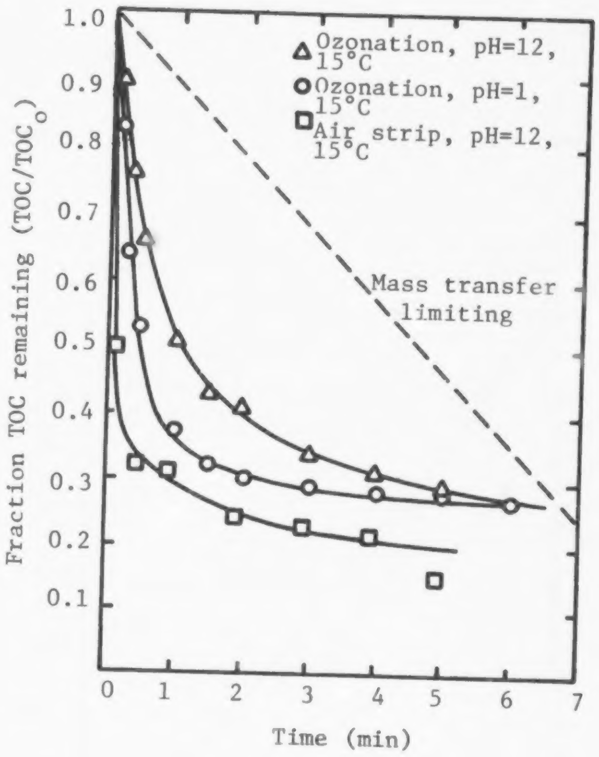


Figure 33. Ozonation of styrene wastewater as a function of time.

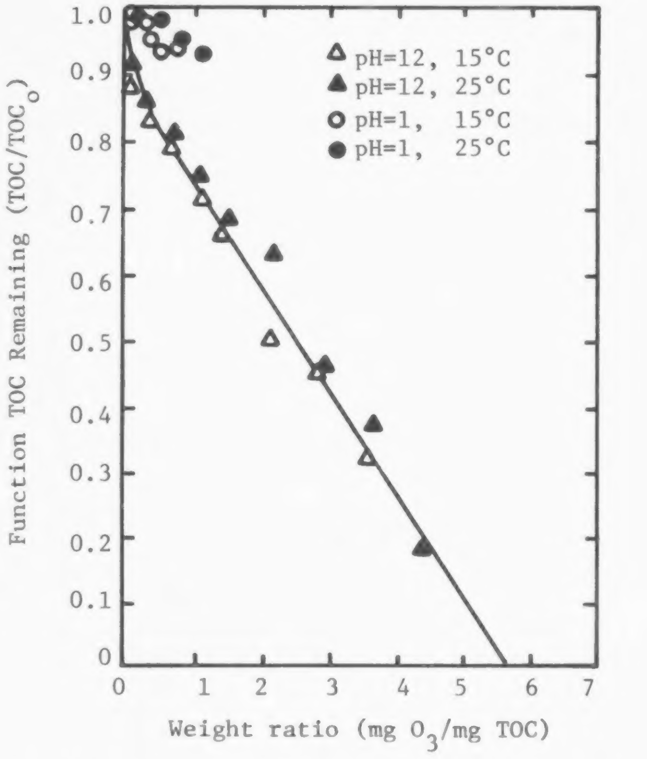


Figure 34. Ozonation of stripped ethylene dichloride wastewater as a function of ozone transferred.

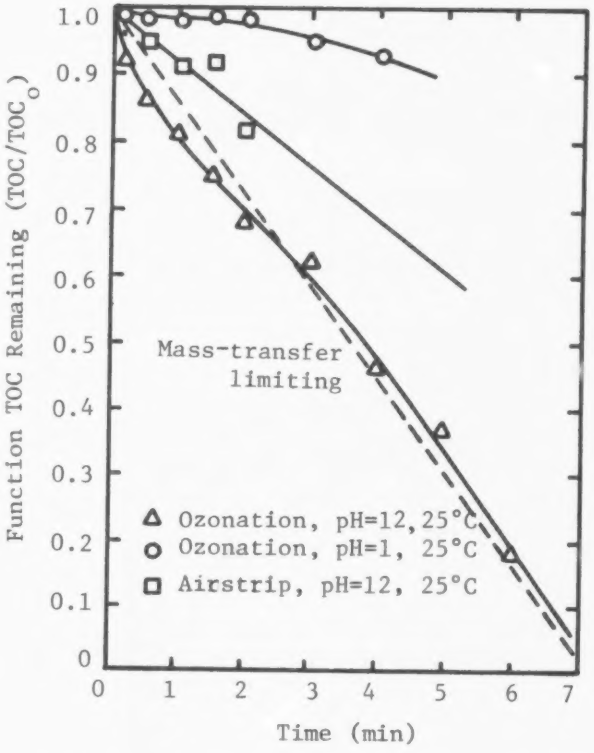


Figure 35. Ozonation of stripped ethylene dichloride wastewater as a function of time.

mg/l (30 percent). The ozonated material was significantly more biodegradable than untreated, stripped EDC wastewater, as shown in Table 100. The TOC reductions averaged 63 percent higher for the ozonated material. An equivalent reduction in BOD was achieved in 48 hr for the ozonated material as was achieved in 72 hr for untreated, steam-stripped EDC. These batch test results were the best obtained during the project.

The combination of steam stripping followed by ozonation produced excellent results; the TOC was reduced from an original value of 1100 to 400 mg/l after stripping to less than 100 mg/l with 3 hr of ozonation. Ozonation showed potential for either complete oxidation or as a pretreatment to biooxidation. The quantity of wastewater will determine the process economics for each ozonation route. A summary of the ozonation study with potential feasibility is given in Table 101.

Ozonation Studies for Reactions of Benzoic Acid, Benzaldehyde, and Styrene

Aqueous solutions of styrene, benzaldehyde, and benzoic acid were ozonated in the semi-batch mode. The ozone feed gas concentration and operating parameters were selected to starve the reaction if it were mass-transfer limiting with an instantaneous reaction. The effect of temperature and solution pH on the individual reaction rates were studied. The reaction rate constant was calculated from the initial 15 min of each test to reduce the effects of competing side reactions between ozone and reaction products. The mass-transfer limiting line was calculated for each test using eq. (19).

$$\frac{N_A}{N_{Ao}} = 1 - \frac{GY_{BF}}{N_{Ao} b_1} t \qquad (19)$$

The stoichiometric mole ratio, b_1, was determined from a plot of the fraction of reactant remaining versus the mole ratio of ozone to the liquid reactant. The moles of ozone transferred into the liquid for reaction was determined by a material balance calculation. The proper reaction regime was determined from comparing the liquid reactant reduction to that predicted with the truly mass-transfer limiting line and by monitoring the ozone concentration in the liquid. The reaction rate constant was evaluated with eq. (20) if the reaction was slow.

$$\frac{N_A}{N_{Ao}} = e^{-\omega_1 t} \qquad (20)$$

where:

$$\omega_1 = \frac{K_1 V \bar{x}_B}{L} \qquad (21)$$

The 5-day biological oxygen demand (BOD_5) was determined on each test stream before and after ozonation. The ratio of BOD_5 to total organic carbon (TOC) gives the oxygen utilized for oxidizing the organic carbon per carbon atom. Comparing the experimental BOD_5 to TOC ratio to theoretical values for complete oxidation gives an indication of the biotreatability of the stream. An ozonation efficiency was calculated for each compound

TABLE 100. SUMMARY OF BATCH STUDY RESULTS FOR STRIPPED EDC WASTEWATER BEFORE AND AFTER OZONATION

	Reactor 1		Reactor 2		Reactor 3		Reactor 4		Reactor 5		Reactor 6	
Time (hours)	0	72	0	72	0	72	0	72	0	72	0	72
Stripped EDC												
F/M	0.05		0.10		0.15		0.20		Airstripped		Baseline	
TOC (mg/1)	75	37	126	38	170	88	175	104	203	106	27	27
TOC Reduction (%)		51		70		48		41		48		0
BOD_5 (mg/1)	87	17	158	30	218	84	298	140	302	163	28	30
BOD_5 Reduction (%)		80		81		61		53		46		0
Ozonated Stripped EDC												
F/M	0.05		0.10		0.15		0.157		Airstripped		Baseline	
TOC (mg/1)	79	19	138	19	193	13	182	44	245	105	22	16
TOC Reduction (%)		76		86		94		76		57		27
BOD_5 (mg/1)	104	<30*	188	33*	250	59	271	68*	408	204*	27	<30*
BOD_5 Reduction (%)		>71		82		76		75		50		0

*Reading taken at 48 hr.

TABLE 101. SUMMARY OF OZONATION AS A PRETREATMENT FOR INDUSTRIAL WASTEWATERS

Stream	TDI	Polyol	Styrene	Stripped EDC
% TOC reduction after three hours of ozonation (initial TOC=100 mg/l)	26%	48%	70%*	82%
Weight ratio of ozone to TOC required for complete oxidation, mg O_3/mg TOC	7.0	7.3	12.5	5.6
pH for best TOC reduction	<3	>10	>10	>10
Observed reaction regime	Reaction rate controlling	Reaction rate controlling (refractory formed)	Reaction rate controlling (slow reaction)	Mass-transfer limiting with a slow reaction
Is ozonation feasible for complete ozidation?	No	No	No	Yes
Did ozonation improve biotreatability?	Yes	Yes	No**	Yes
Is ozonation feasible as pretreatment to biooxidation?	Yes	Questionable (Refractory formed)	No	Yes

---

[*] Initial TOC reduction was predominantly from airstripping.

[**] Styrene is biotreatable before ozonation.

ozonated by dividing the time required for complete oxidation based on mass-transfer limited basis by the actual time required.

Aqueous Benzoic Acid Solution--

Benzoic acid solutions were prepared with an average concentration of 300 mg/l. The stoichiometric ratio for the disappearance of benzoic acid was found to be approximately 4 moles of ozone per mole of benzoic acid by extrapolating the data for the first 15 min of reaction in Figure 36. This value of b_1 was substituted into eq. (19) to calculate the mass-transfer limiting line.

The effect of temperature on the benzoic acid oxidation was evaluated first with Figure 37 showing the benzoic acid reduction as a function of time at 15° and at 25°C. The benzoic acid reduction at either temperature deviates from the mass-transfer limiting line. Rate constants of 1.95×10^6 Kg mole/m^3 min and 3.43×10^6 Kg mole/m^3 min were calculated at 15° and at 25°C using eq. (22):

$$-\ln(1-\zeta) = \omega_1 t \qquad (22)$$

where ω is the reaction rate modulus and ζ is the fraction of liquid reactant converted.

The increase in the reaction rate was offset by a decrease in ozone solubility at the higher temperature. The mole fraction of ozone in the liquid was calculated from a material balance to be 0.49×10^{-6} and 0.23×10^{-6} for 15° and 25°C, respectively. The liquid ozone concentration could not be measured directly due to interference of the benzoic acid on the potassium iodide method.

The benzoic acid oxidation was studied at pH values of 2, 4, and 11 at 25°C. The effect of solution pH on the reaction rate was dramatic as the reaction became mass-transfer limited at pH 11. The data are shown in Figure 38 for the fraction of benzoic acid remaining as a function of time. The slowest rate constant was 9.84×10^5 Kg mole/m^3 min for an acid solution (pH 2). A minimum reaction rate was estimated for the mass-transfer limited reaction at pH 11 by combining the mass-transfer limited equation with the slow reaction equation. The estimated minimum reaction rate constant to maintain a truly mass-transfer limited system was 8.01×10^7 Kg mole/m^3 min.

The benzoic acid reduction line at pH 11 begins to deviate from the mass-transfer limiting line after 10 min of ozonation, but the reaction was starved for ozone a total of 25 to 30 min. This indicates the high pH also increased the reaction rate of the benzoic acid oxidation products which were competing with benzoic acid for the ozone. After 30 min of ozonation, ozone was detected in the exit gas, indicating that some refractor reaction products were being produced, and that the slower reactions were beginning to control the system. The benzoic acid reduction was significantly slowed after 85 percent of the compound was oxidized. This decrease in benzoic acid reduction at the lower concentrations proves the reaction is dependent on the benzoic acid concentration.

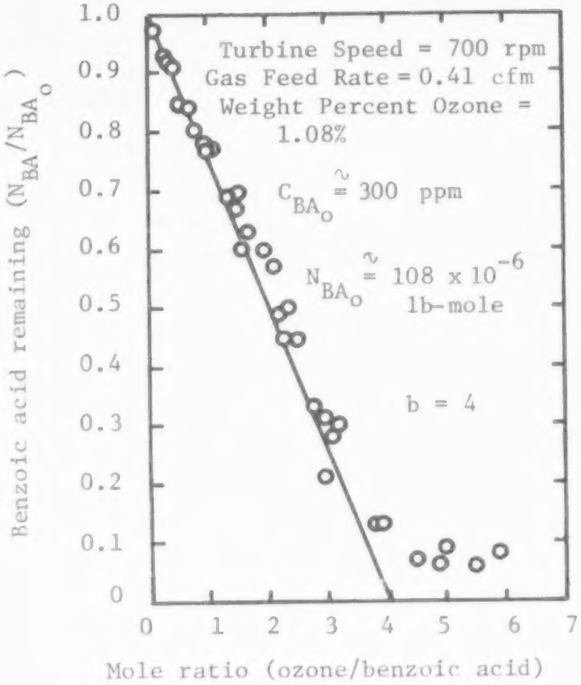


Figure 36. Determination of stoichiometric ratio for the ozonation of benzoic acid.

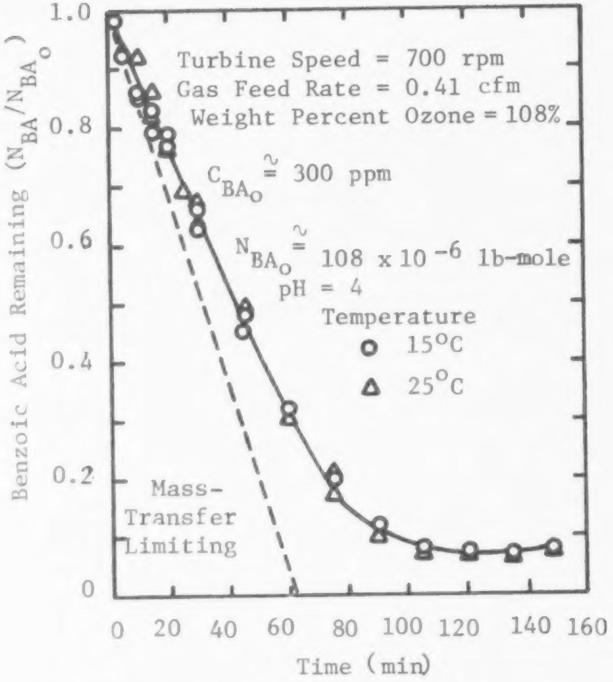


Figure 37. Effect of temperature on the ozonation of benzoic acid in aqueous solution.

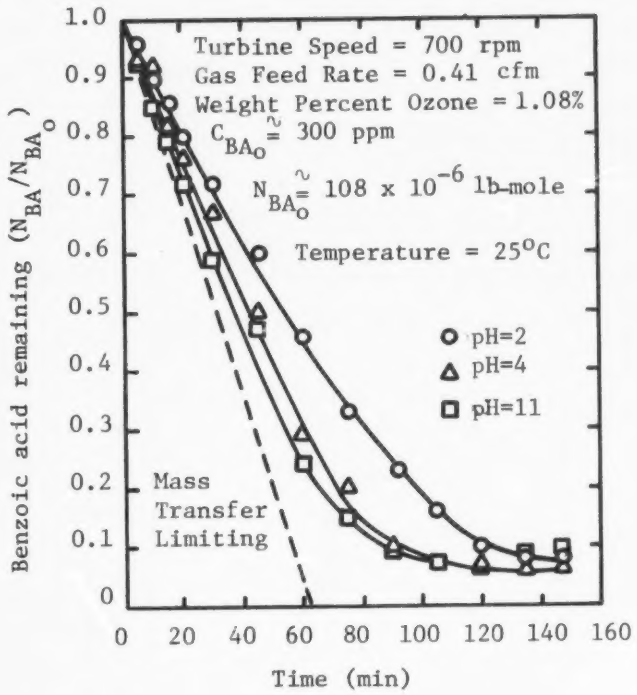


Figure 38. Effect of pH on the ozonation of benzoic acid in aqueous solution.

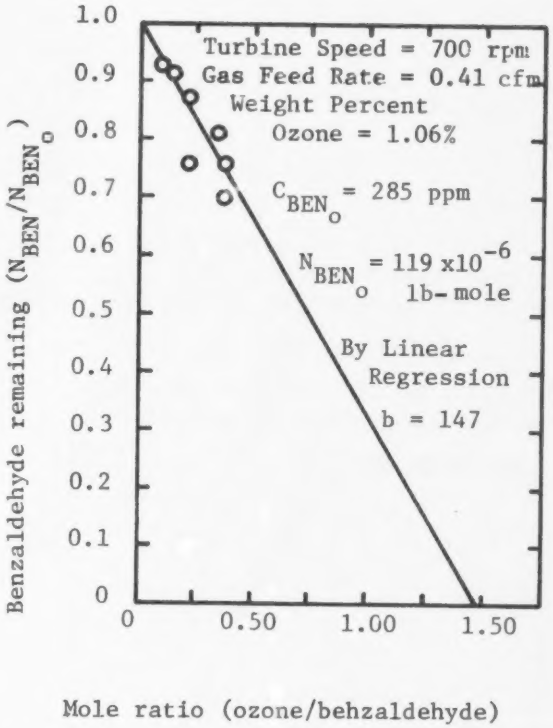


Figure 39. Determination of stoichiometric ratio for the ozonation of benzaldehyde.

The increased oxidation rate with a high pH was attributed to the formation of hydroxy radicals (OH). The decomposition of ozone in the liquid phase is greatly increased at high pH values. Previous studies (14,16,17,22,24) have shown that other ozonation reactions proceed faster under basic conditions.

Benzoic acid is fairly biodegradable; the experimental BOD_5 to TOC ratio was 2.46, as compared to a theoretical value of 3.05. The ratio was increased as the ozonation proceeded to 2.89 after 150 min of ozonation. A summary of the benzoic acid ozonation data is given in Table 102. A low efficiency for benzoic acid oxidation was a result of the rapid decrease in benzoic acid reduction at low residual concentrations.

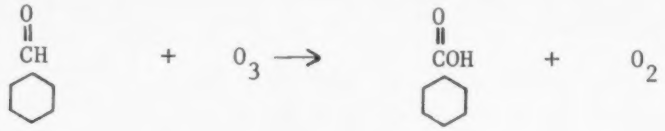
TABLE 102. SUMMARY OF THE OZONATION REACTION STUDY FOR BENZOIC ACID, BENZALDEHYDE AND STYRENE IN AQUEOUS SOLUTIONS

	pH=4		pH=2	pH=11
Compound	15°C	25°C	25°C	25°C
Benzoic Acid				
Reaction Regime	a	a	a	b → a
Reaction Rate Constant, $\frac{\text{Kg mole}}{\text{m}^3\ \text{min}} \times 10^{-4}$	194.88	343.04	98.24	8000
Ozonation Efficiency, %	47.7	48.4	41.8	55.2
Benzaldehyde				
Reaction Regime	a	a	a	b → a
Reaction Rate Constant, $\frac{\text{Kg mole}}{\text{m}^3\ \text{min}} \times 10^{-4}$	213.28	419.68	154.08	3901.60
Ozonation Efficiency, %	24.6	22.6	21.8	25.5
Styrene				
Reaction Regime	b	b	b	b
Reaction Rate Constant, $\frac{\text{Kg mole}}{\text{m}^3\ \text{min}} \times 10^{-4}$	>8000	>8000	>8000	>8000
Operation Efficiency, %	100	100	100	100

[a] Mass-transfer limiting with a slow reaction.
[b] Mass-transfer limiting with an instantaneous reaction.
[c] Reaction rate controlled.

Aqueous Benzaldehyde Solution--

The benzaldehyde oxidation followed a pattern similar to that of benzoic acid. The average initial benzaldehyde concentration was 285 mg/l. The stoichiometric mole ratio for benzaldehyde was calculated to be 1.7 moles of ozone per mole of benzaldehyde by extrapolating the initial benzaldehyde reduction data with linear regression in Figure 39. This deviates from the ratio predicted by the proposed reaction of benzaldehyde to benzoic acid in eq. (23).



(23)

The data are extremely scattered because benzoic acid has a reaction rate constant of the same magnitude as the benzaldehyde and competes for the ozone transferred into the liquid.

The temperature effect for benzaldehyde oxidation was similar to that for the benzoic acid oxidation; the calculated rate constant was doubled for the 10-degree increment while the benzaldehyde reduction rate remained the same. The calculated reaction rates were 13.33 lb mole/ft^3 min at 15°C and 26.23 lb mole/ft^3 min at 25°C. The increase in reaction rate was again offset by the ozone liquid mole fraction being halved from 0.5×10^{-6} to 0.24×10^{-6} at the respective temperatures. The system was mass-transfer controlled with a slow reaction regime; the ozone never reached equilibrium. The deviation from the mass/transfer limiting line is evident in Figure 40.

Figure 41 shows the benzaldehyde reduction approached the mass-transfer limiting line at pH 11. The benzaldehyde reaction was truly mass-transfer limited for the initial 5 min. Unlike the benzoic acid ozonation, a concentration of ozone was detected in the liquid after the initial 5 min, shifting the reaction to the mass-transfer limited with a slow reaction regime. The stoichiometric ratio and the early deviation from being mass-transfer limited suggest an intermediate was formed between the benzaldehyde and the benzoic acid. The mole fraction of ozone in the liquid dropped from 0.06×10^{-6} to 0.03×10^{-6} as the benzoic acid continued to be produced and reacted at a faster rate than the benzaldehyde. The rate constants were calculated for the pH extremes using eq. (20). These values were 1.54×10^{6} Kg mole/m^3 min for a solution pH of 2 and 3.91×10^{7} Kg mole/m^3 min pH 11. The benzaldehyde relative biodegradability is shown with an experimental BOD_5 to TOC ratio of 2.30 compared to a theoretical value of 2.85. The ozonation again increased the ratio to a value of 2.66 after 150 min.

Aqueous Styrene Solution--

The ozonation of styrene in aqueous solution was difficult to evaluate because the styrene was easily air stripped from solution and very insoluble in water. The average initial concentration achieved was 130 mg/l. The styrene ozonation data are shown in Figure 42. The ozonated styrene reduction line fell below the mass-transfer limiting line which is not feasible. Therefore, air stripping tests were performed which showed the styrene was air stripped from the solution. The air stripping curve in Figure 42 was used to correct the ozonation data by compensating for the styrene air stripped from the solution and not available for oxidation. The styrene reduction data for the various pH solutions and temperatures were in agreement with the mass-transfer limiting with an instantaneous reaction line after being corrected for air stripping as shown in Figure 35. The mass-transfer

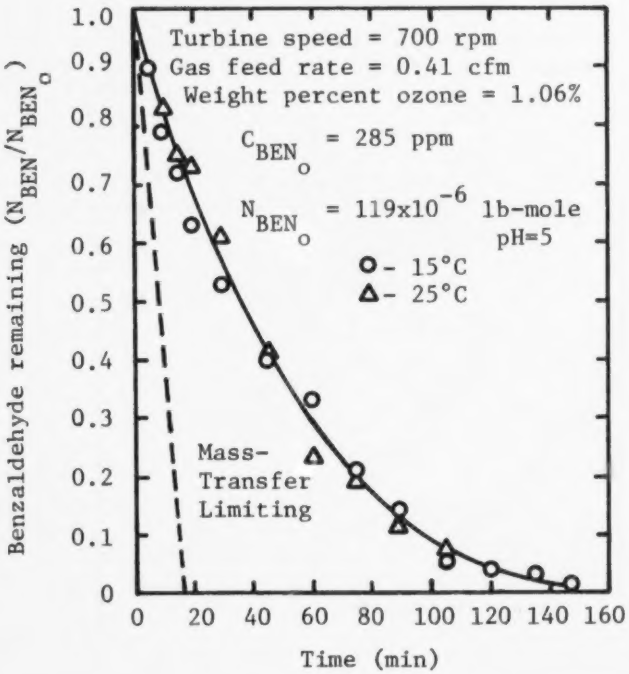


Figure 40. Effect of temperature on the ozonation of benzaldehyde in aqueous solution.

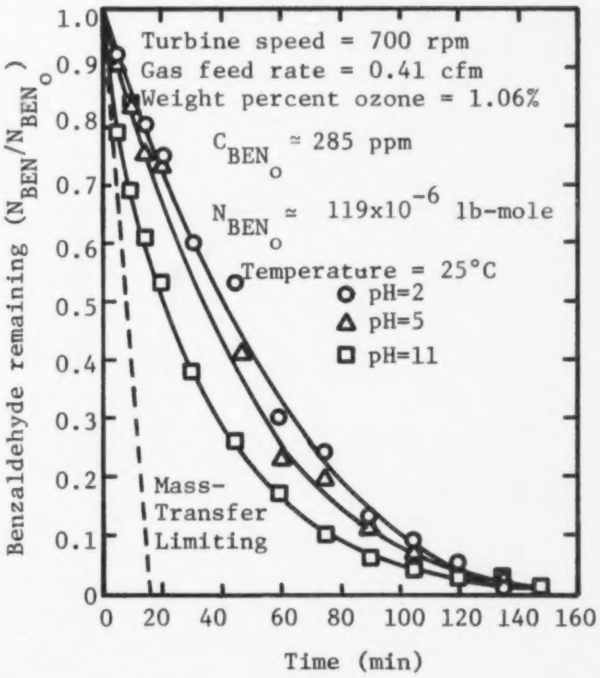


Figure 41. Effect of pH on the ozonation of benzaldehyde in aqueous solution.

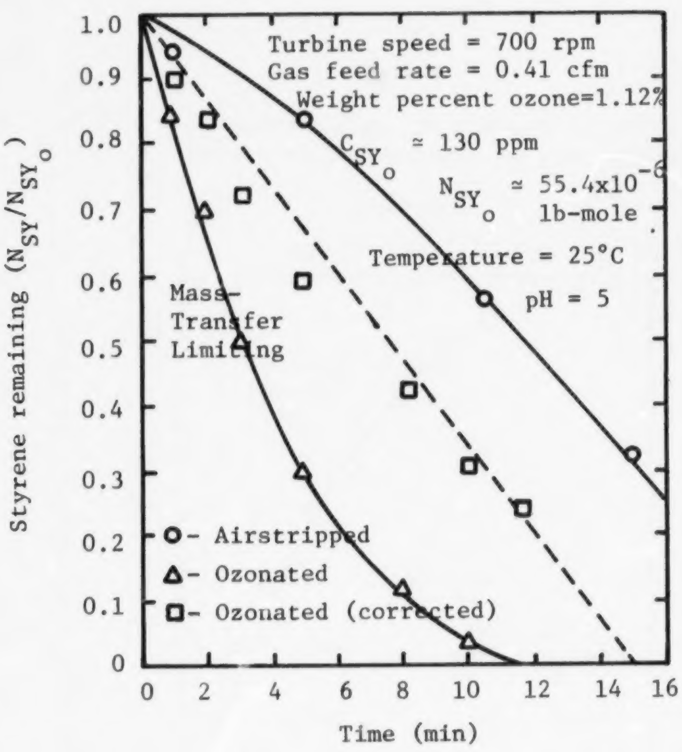


Figure 42. Ozonation in styrene in aqueous solution and the effect of air-stripping on the system.

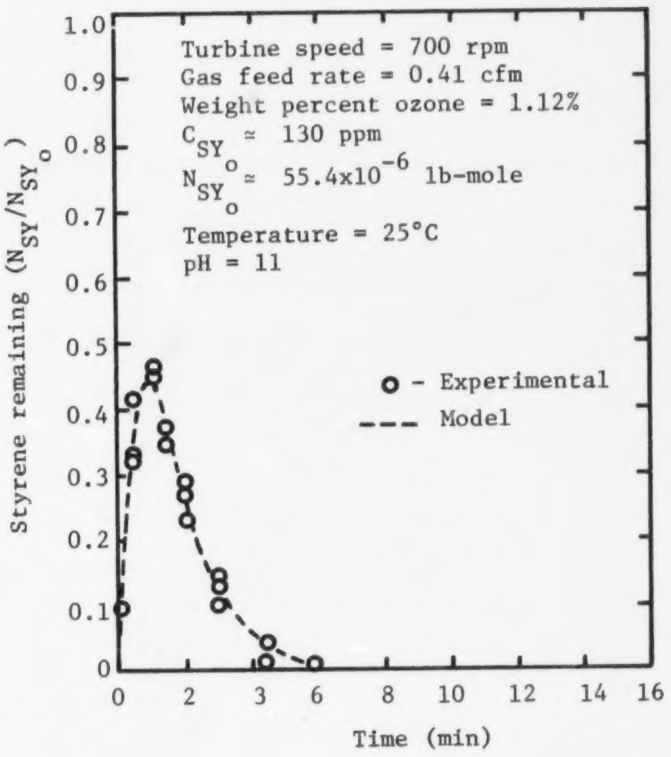


Figure 43. Application of the model for benzaldehyde from the ozonation of styrene in aqueous solution.

limiting and reaction rate limiting equations were combined to estimate a minimum reaction rate constant of 8.01 x 10^7 Kg mole/m^3 min. The method described by Levnspiel (8) was used to estimate a reaction rate constant of 8.87 x 10^7 Kg mole/m^3 min.

The styrene rate constant was verified with the use of the model developed for benzaldehyde. The various rate constants determined for benzaldehyde at the different operating conditions and the styrene rate constant were used to calculate the fraction of benzaldehyde as a function of time. Figure 43 is a comparison of the model prediction, depicted with the dotted line, with experimental data for a solution pH of 11 and a temperature of 25°C. The model prediction correlated well with the experimental data supporting the rate constants calculated.

Styrene is relatively nonbiodegradable; the experimental BOD_5 to TOC ratio was 0.47 as compared to the theoretical value of 3.33. Ozonation greatly improved the biotreatability, as the ratio was increased toward the benzoic acid ratio after 90 min of ozonation and finally 2.69 after 150 min. The total organic carbon content was decreased from 130 to 39 mg/l for a 70 percent reduction. The ozonation efficiency was 100 percent; all the tests were mass-transfer limited.

Reaction Study Summary

Ozonation was found to improve the biotreatability of water containing styrene by transforming the styrene to biodegradable compounds such as benzoic acid. The BOD_5 to TOC ratio was improved for all the compounds studied as shown in Table 103. The styrene solutuion ratio was significantly improved after 150 min of ozonation from 0.41 to 2.69.

TABLE 103. SUMMARY OF FIVE-DAY BIOLOGICAL OXYGEN DEMAND TO TOTAL ORGANIC CARBON RATIO DATA FOR REACTION SOLUTIONS

Solution	BOD_5/TOC		
	Theoretical	Pre-Ozonation	Post-Ozonation[a]
Benzoic Acid	3.05	2.46	2.89
Benzaldehyde	2.86	2.30	2.66
Styrene	3.33	0.47	2.69

[a] Ozonation performed at solution pH of 5 and a temperature of 25°C for 150 min.

The complete oxidation of styrene may be costly as some reaction products react more slowly, but the initial oxidation of styrene to benzaldehyde was rapid. The ozonation of styrene was truly mass-transfer limited with an estimated reaction rate constant of 8.87 x 10^7 Kg mole/m^3 min. The rate constant was verified, as the model accurately predicted the benzaldehyde concentration from the ozonation of styrene using the various rate constants for benzaldehyde and the rate constant of styrene.

The ozonations of benzaldehyde and benzoic acid were affected by both solution pH and temperature. Benzaldehyde and benzoic acid ozonations were mass-transfer limited with a slow reaction under acidic conditions. But at a pH of 11, the reactions became truly mass-transfer limited. The higher oxidation rates are related to the increased hydroxy radical formation from ozone under basic conditions. A 10-degree increase in temperature produced a higher reaction rate constant which was offset by lower ozone liquid concentrations. The overall net effect was equivalent reduction rates for both temperatures. None of the reactions were truly reaction-rate controlled as the ozone never reached its solubility limit.

The reaction was proved to be bimolecular since the reactions were dependent on both reactant concentrations. The lower ozone liquid concentration reduced the reduction in the temperature study while the liquid reactant reduction was slowed at lower concentrations. A summary of the ozonation studies including the proper reaction regime, rate constant, and ozonation efficiency for the oxidation of the compounds was presented in Table 102.

ECONOMIC EVALUATION

Ozone as Pretreatment for Styrene Plant Wastewater

An investigation was made of the economics of treating a process effluent containing aromatics, principally styrene, as the contaminant. The capital cost of the installation and manufacturing costs are shown in Table 104.

TABLE 104. CAPITAL AND OPERATING COST FOR OZONE PRETREATMENT

Capital Cost		
Ozonator	115-kg/day ozonators	$320,000
Reactor	Stainless steel tank with agitator and sparger	70,000
Pumps, piping and instrumentation		60,000
Installation		100,000
Total		$550,000
Operating Cost Per Year		
Utilities	10 kw/kg of ozone at $0.03/kwh	$150,000
Manpower	5 men at $10/hr	100,000
Maintenance at 6% of capital		33,000
Insurance and Taxes at 2% of capital		12,000
G&A at 2% of capital		12,000
Chemicals and Supplies		12,000
Depreciation - 10-year straight line		55,000
Interest at 9%		2,500
Start-up cost		24,000
Total Treatment Cost		$400,000

This ozonator was to be added as a pretreatment step to a system already biotreating the process effluent. The ozonation equipment was designed to treat wastewater from a styrene plant containing 300 mg/l TOC of which 200 mg/l was styrene. The reactor was sized to treat 600 liters/min wastewater flow. The ozonators were designed to produce an excess of 20 percent of the ozone required to oxidize the styrene to benzaldehyde.

Economics of Pretreatment

Table 105 shows the cost of ozone pretreatment of a styrene plant effluent with the previously indicated contaminant loading. If a manufacturing value of 22¢/kg is assigned to the styrene product, this pretreatment cost represents 8 percent of the value, and is somewhat high for this manufacturing process.

TABLE 105. COST OF PRETREATMENT

Water Pretreated (liters/min)	600
Water Pretreated (liters/yr)	270,000,000
Cost of Pretreatment (cents/gallon)	0.015
Total Styrene Production (kg/yr)	225,000,000
Cost of Pretreatment (cents/kg of styrene)	0.18

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APPENDIX

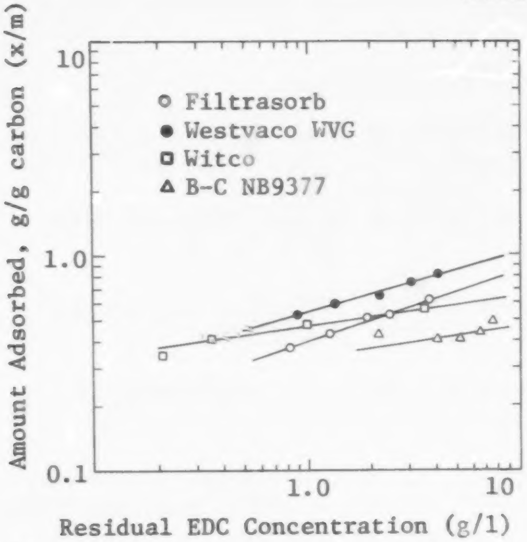

Figure 1A. Ethylene dichloride isotherms for stream 041A.

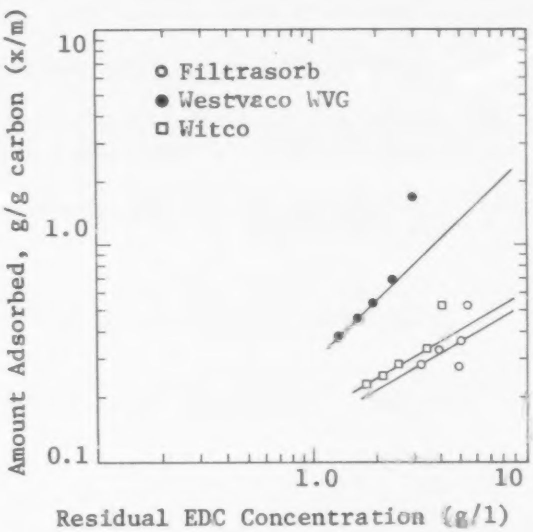

Figure 2A. Ethylene dichloride isotherms for stream 221A.

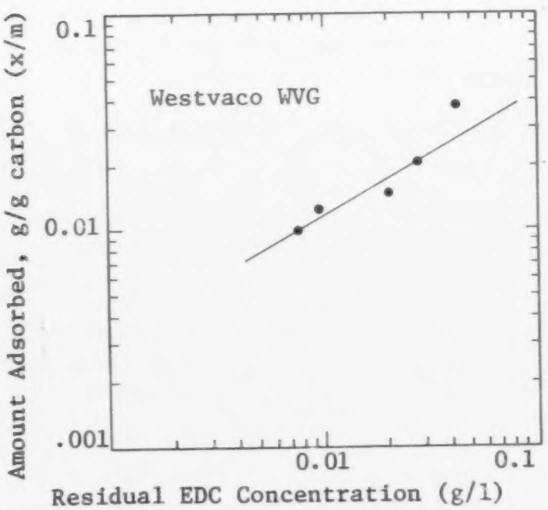

Figure 3A. Ethylene dichloride isotherms for stream 161A.

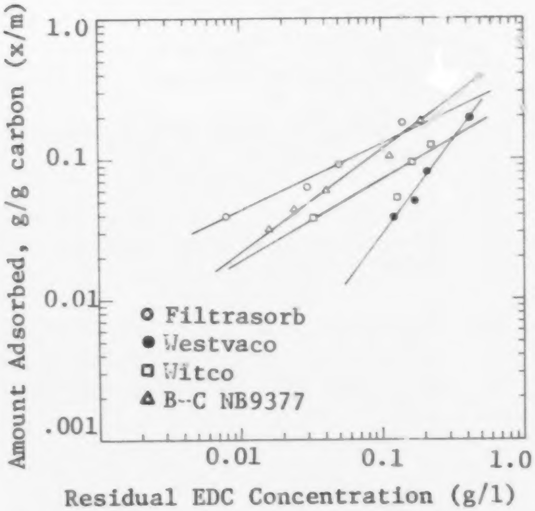

Figure 4A. Ethylene dichloride isotherms for stream 041A (lower concentration range).

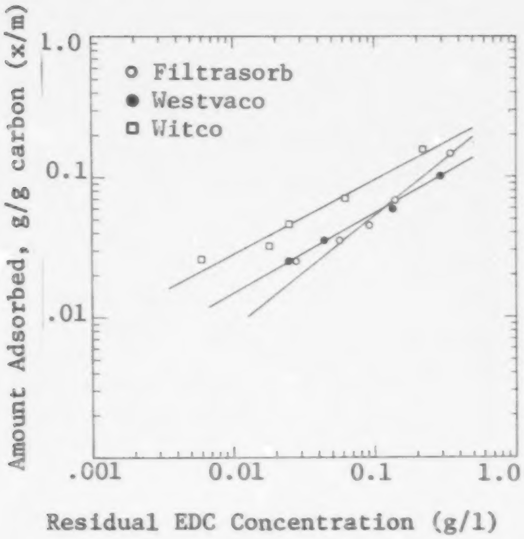

Figure 5A. Ethylene dichloride isotherm for stream 221A (lower concentration range).

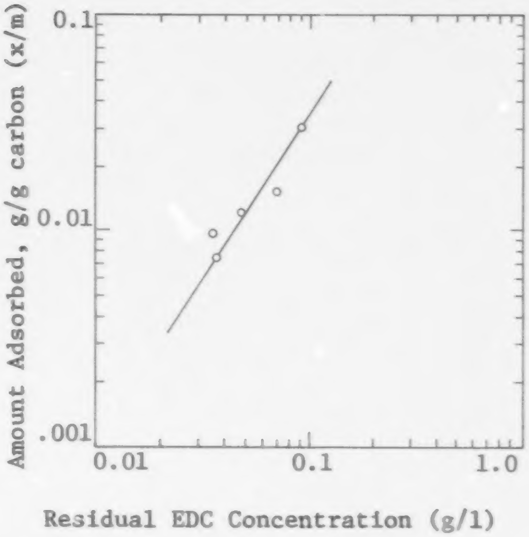

Figure 6A. Ethylene dichloride iostherm for stream 161A (upper concentration range).

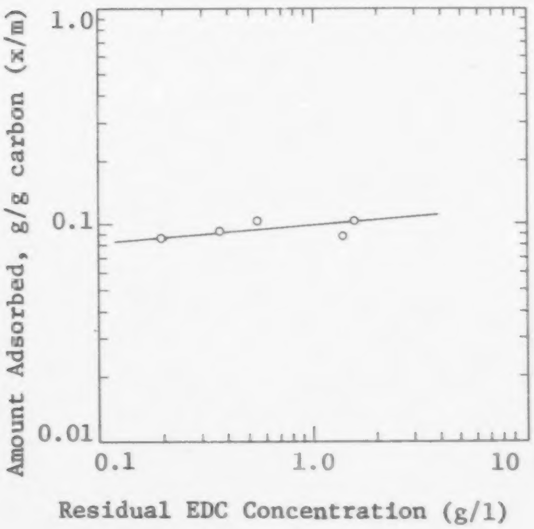

Figure 7A. Ethylene dichloride isotherm for stream 041A.

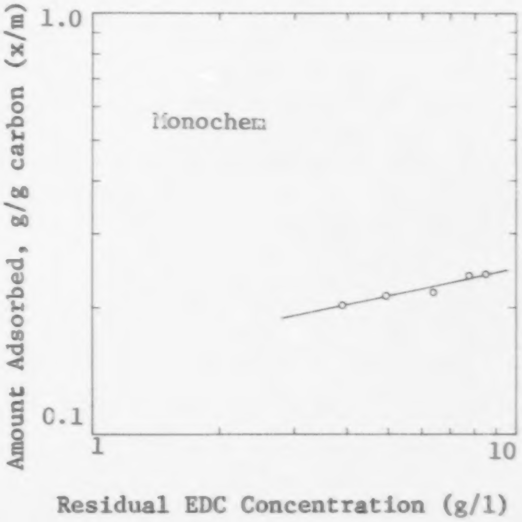

Figure 8A. Ethylene dichloride isotherm for stream 221A.

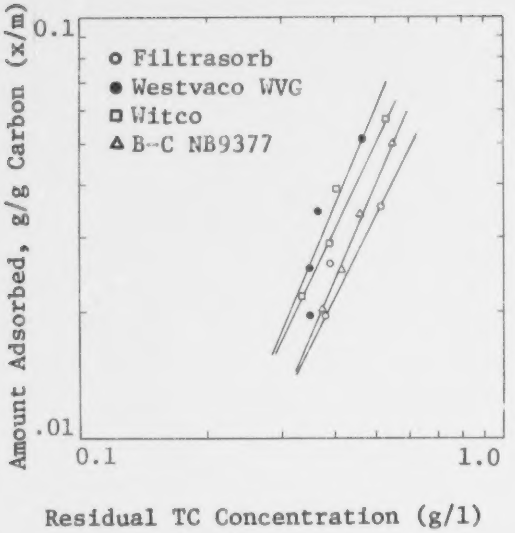

Figure 9A. Total carbon isotherm for stream 041A.

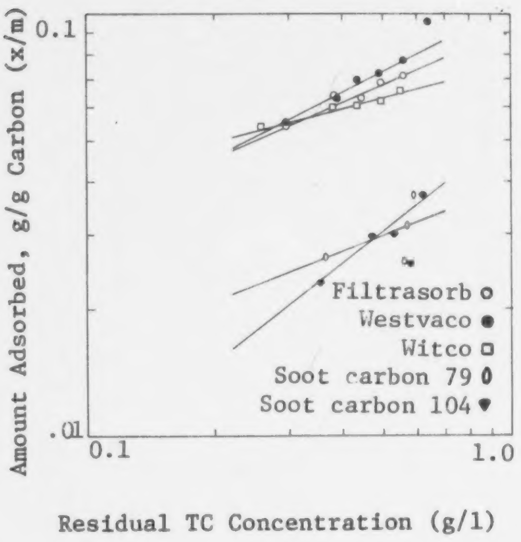

Figure 10A. Total carbon isotherm for stream 221A.

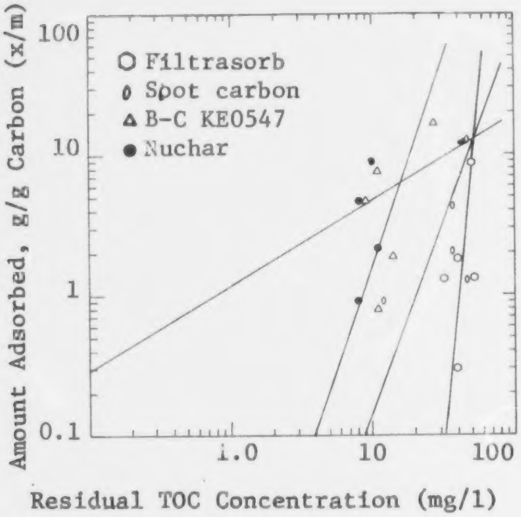

Figure 11A. Total organic carbon isotherm for stream 351A.

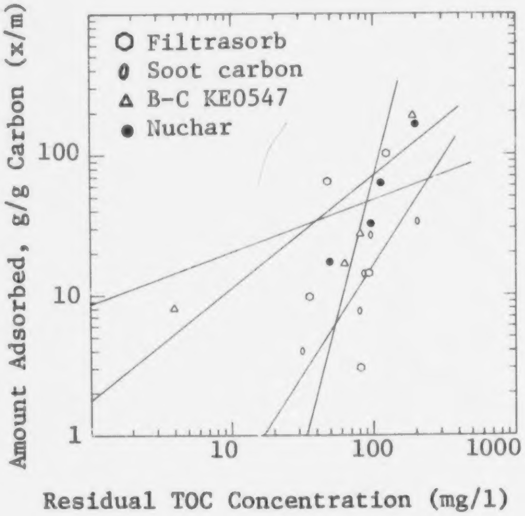

Figure 12A. Total organic carbon isotherm for stream 231A.

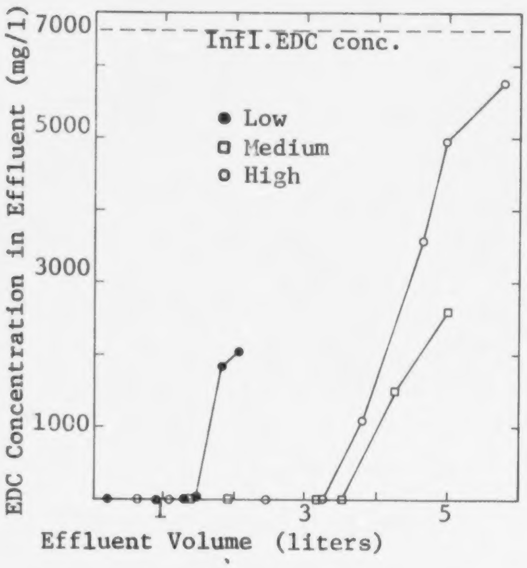

Figure 13A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

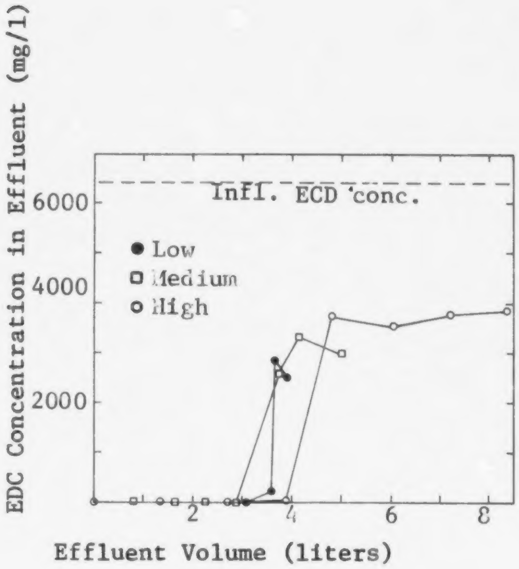

Figure 14A. Breakthrough curve for laboratory continuous adsorption study with Filtrasorb-400 carbon.

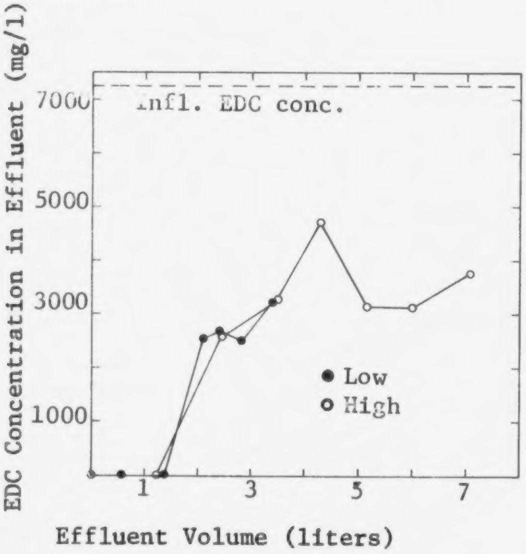

Figure 15A. Breakthrough curve for laboratory continuous adsorption study with Monochem soot carbon.

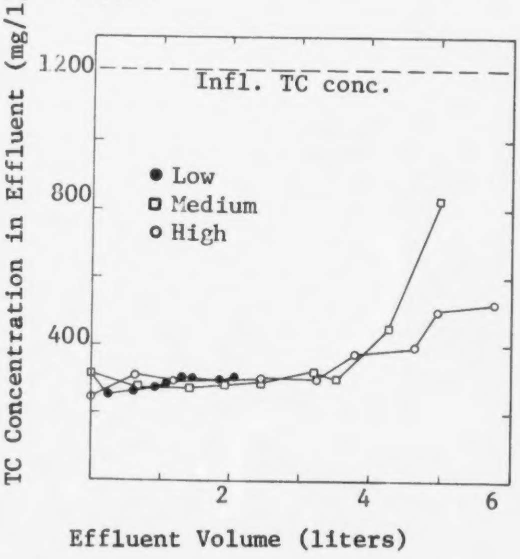

Figure 16A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVC carbon.

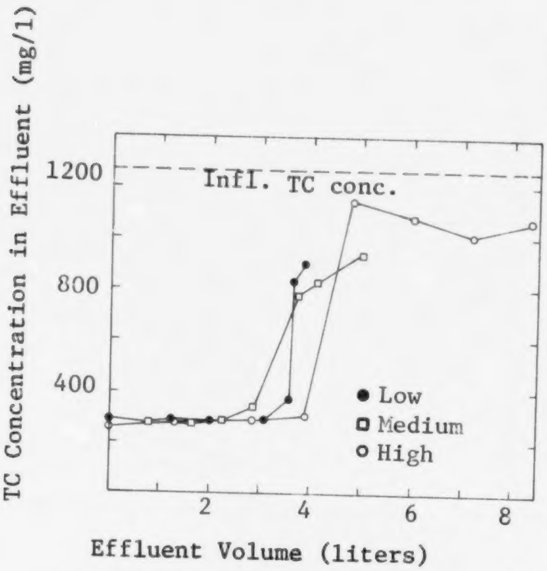

Figure 17A. Breakthrough curve for laboratory continuous adsorption study with Filtrasorb-400 carbon.

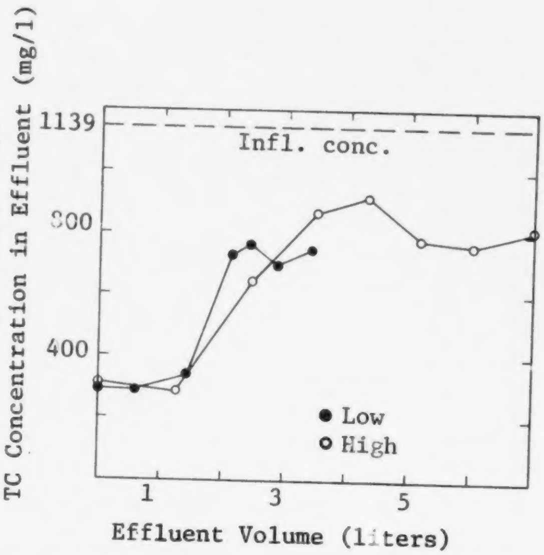

Figure 18A. Breakthrough curve for laboratory continuous adsorption study with Monochem soot carbon.

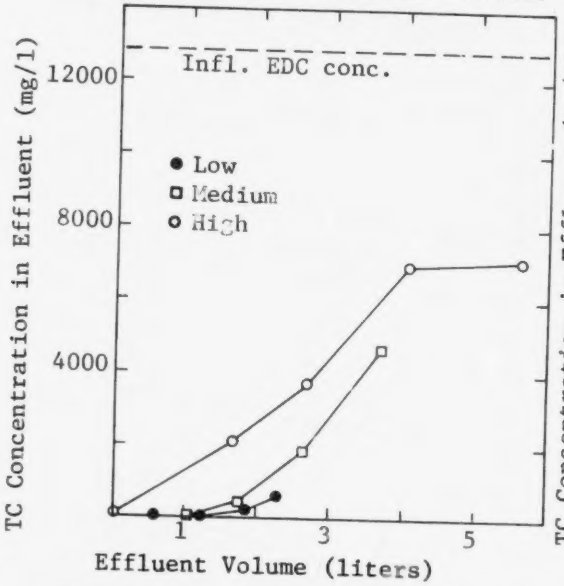

Figure 19A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

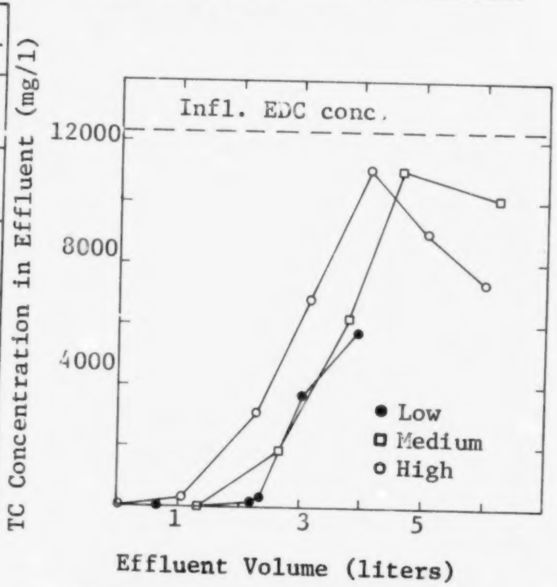

Figure 20A. Breakthrough curve for laboratory continuous adsorption study with Filtrasorb-400 carbon.

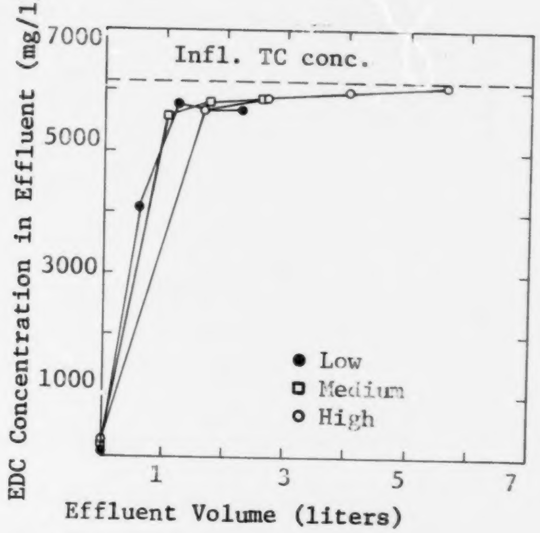

Figure 21A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

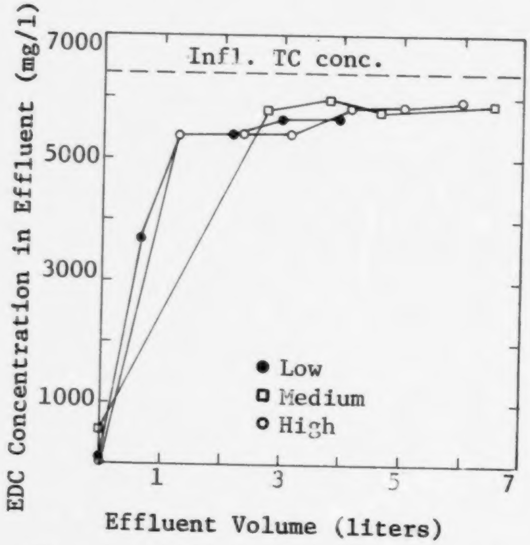

Figure 22A. Breathrough curve for laboratory continuous adsorption study with Filtrasorb-400 carbon.

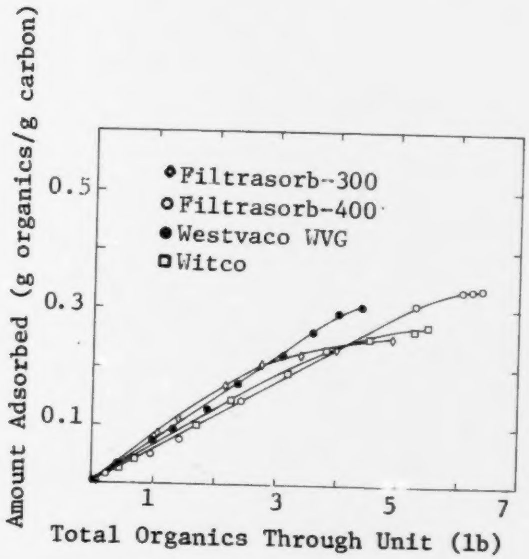

Figure 23A. Field study of various activated carbons.

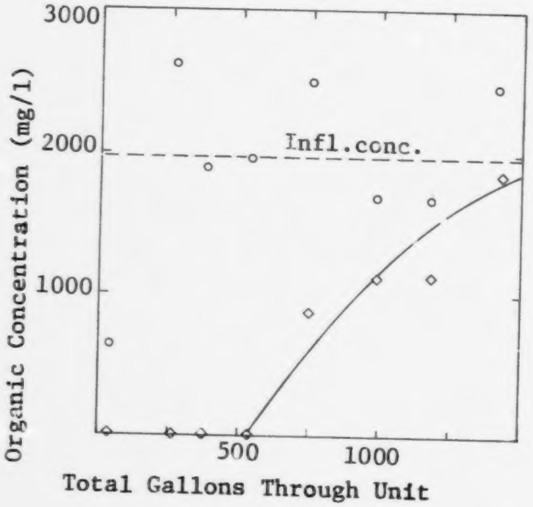

Figure 24A. Breakthrough curve for field study with Filtrasorb-300 carbon, stream 221A.

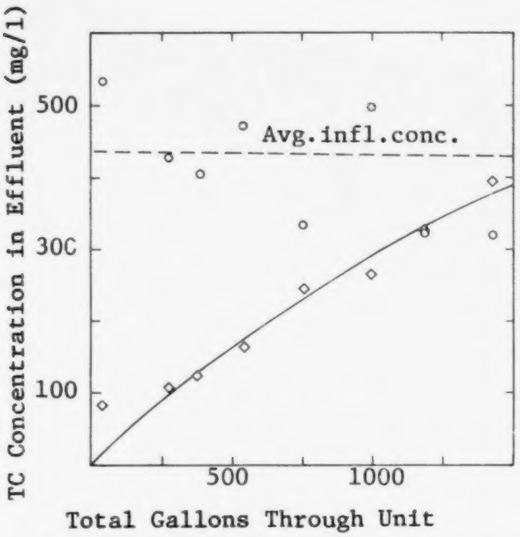

Figure 25A. Breakthrough curve for field study with Filtrasorb-300 carbon, stream 221A.

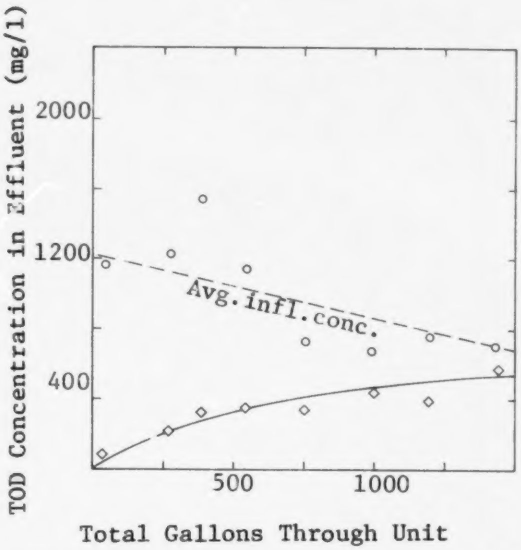

Figure 26A. Breakthrough curve for field study with Filtrasorb-300 carbon, stream 221A.

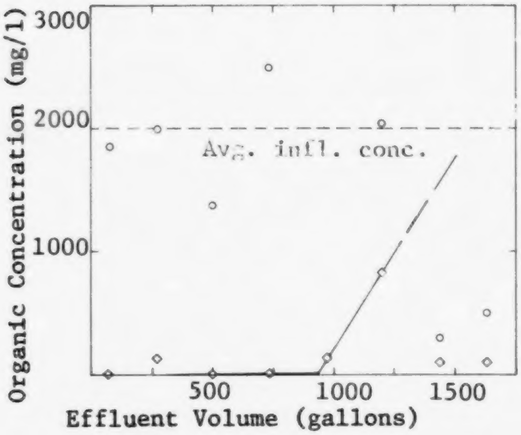

Figure 27A. Breakthrough curve for laboratory continuous adsorption study with Filtrasorb-300 carbon.

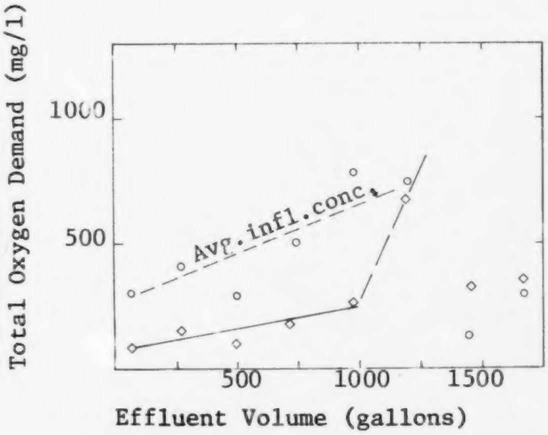

Figure 28A. Breakthrough curve for laboratory continuous adsorption study with Filtrasorb-400 carbon.

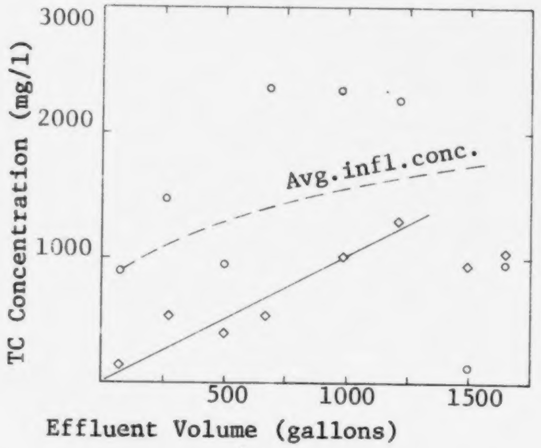

Figure 29A. Breakthrough curve for laboratory continuous adsorption study with Filtrasorb-400 carbon.

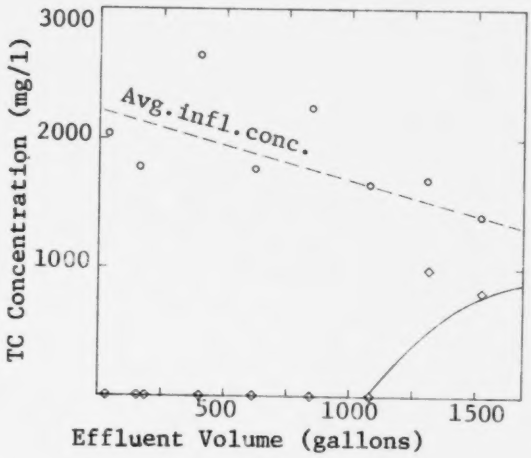

Figure 30A. Breakthrough curve for laboratory continuous adsorption study with WITCO carbon.

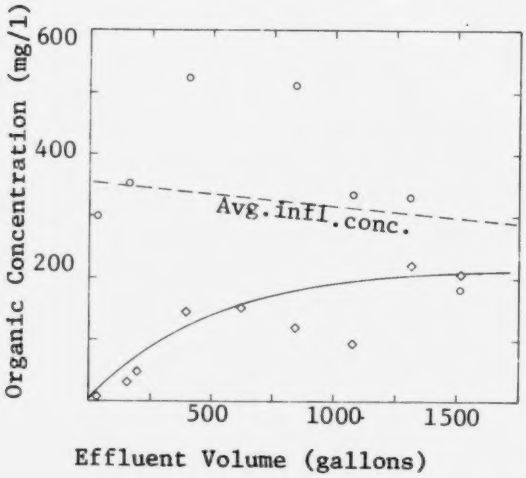

Figure 31A. Breakthrough curve for laboratory continuous adsorption study with WITCO carbon.

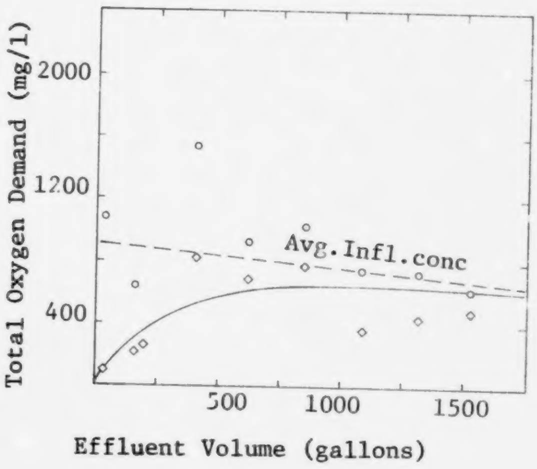

Figure 32A. Breakthrough curve for laboratory continuous adsorption study with WITCO carbon.

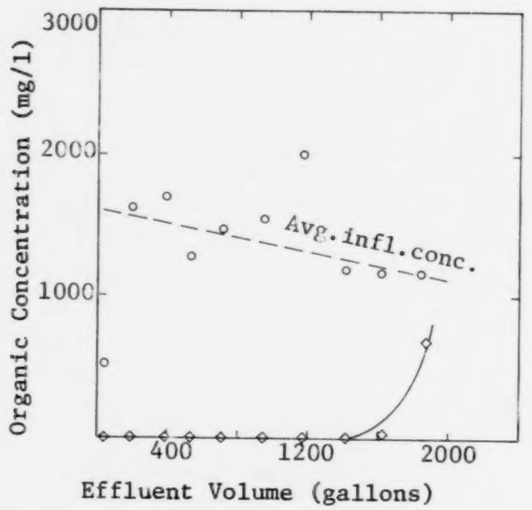

Figure 33A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

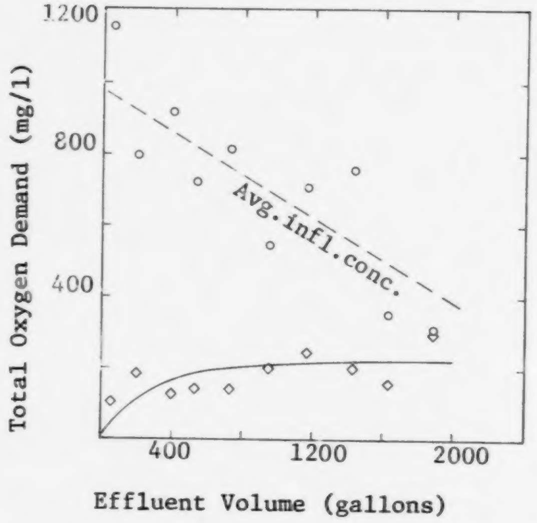

Figure 34A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

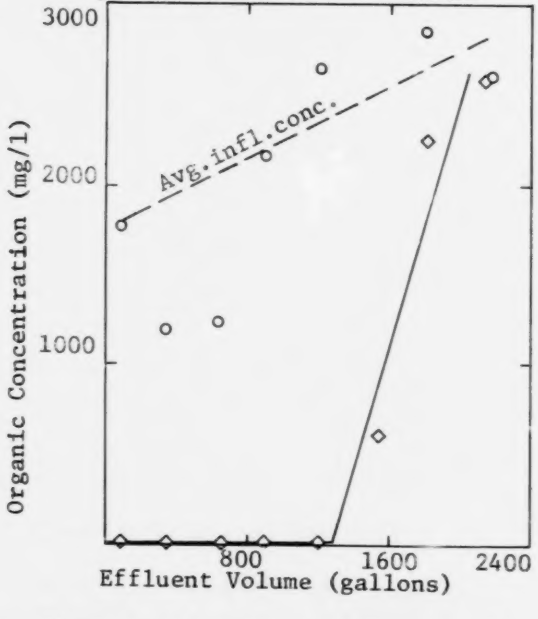

Figure 35A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

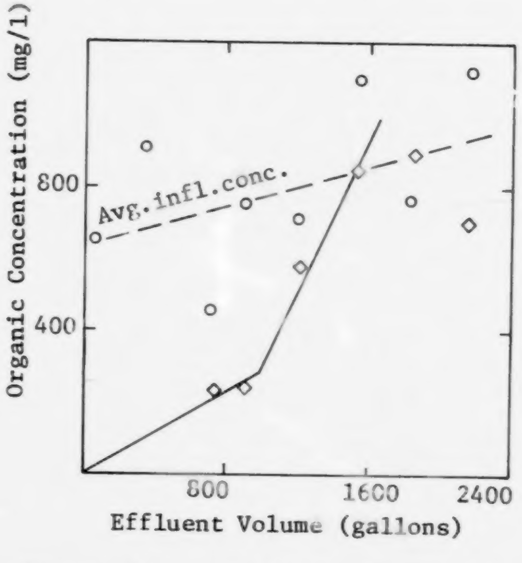

Figure 36A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

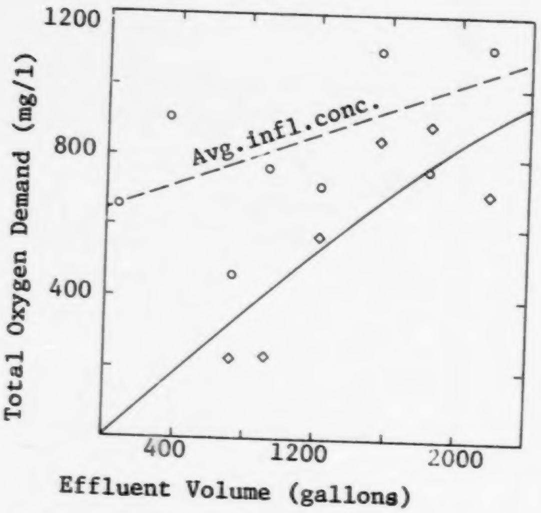

Figure 37A. Breakthrough curve for laboratory continuous adsorption study with Westvaco WVG carbon.

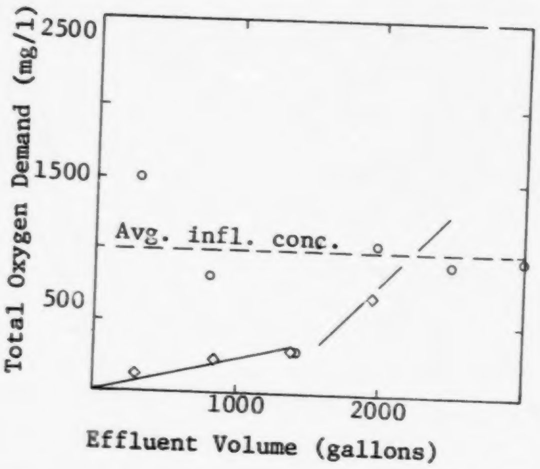

Figure 38A. Breakthrough curve for laboratory continuous adsorption study.

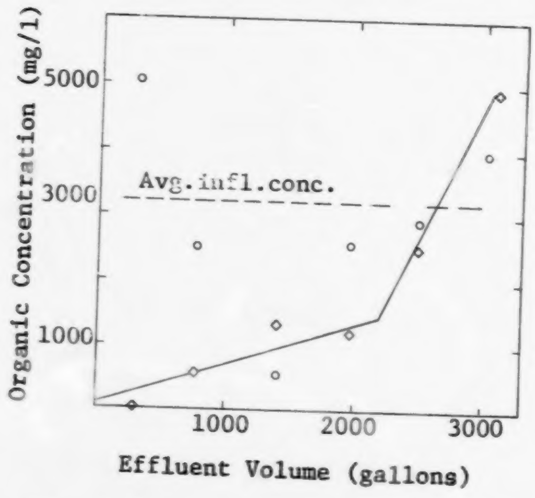

Figure 39A. Breakthrough curve for laboratory continuous adsorption study.

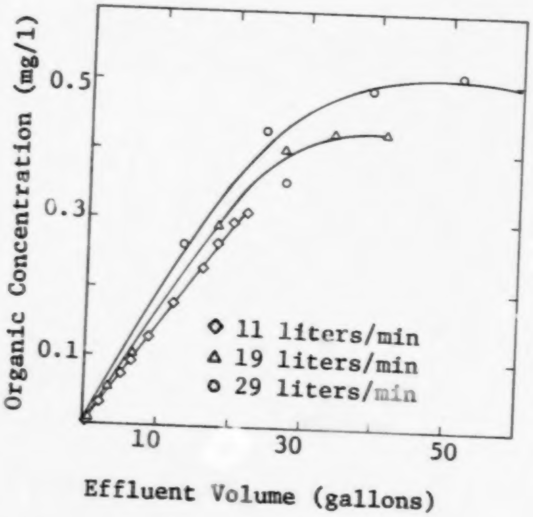

Figure 40A. Flow rate effects of best activated carbon.

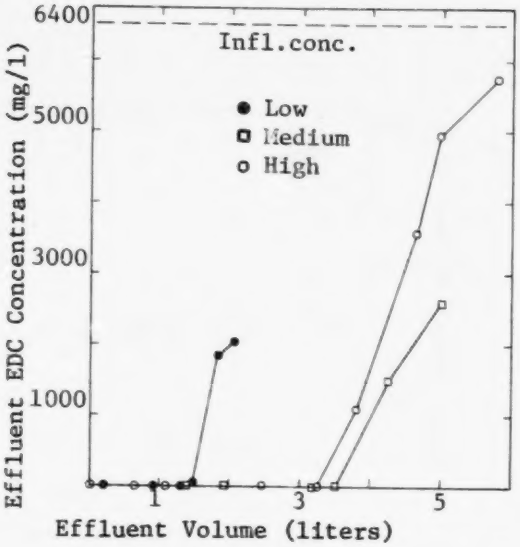

Figure 41A. Breakthrough curve for stream 041A with WVG carbon.

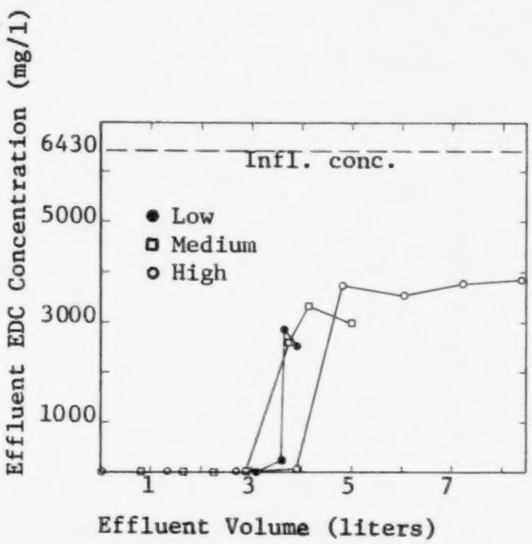

Figure 42A. Breakthrough curve for stream 041A with Filtrasorb-400 carbon (solute: EDC).

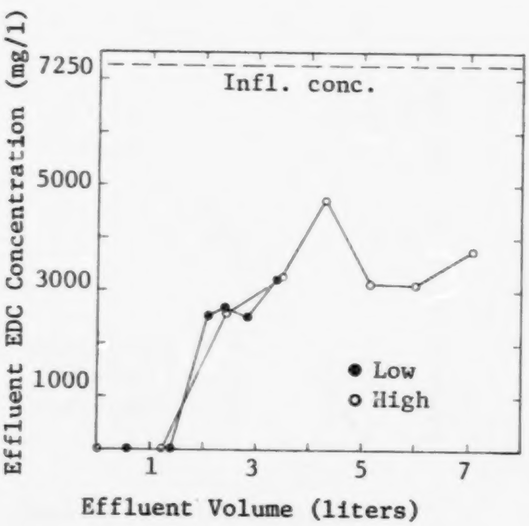

Figure 43A. Breakthrough curve for stream 041A with Monochem carbon, run #104 (solute: EDC).

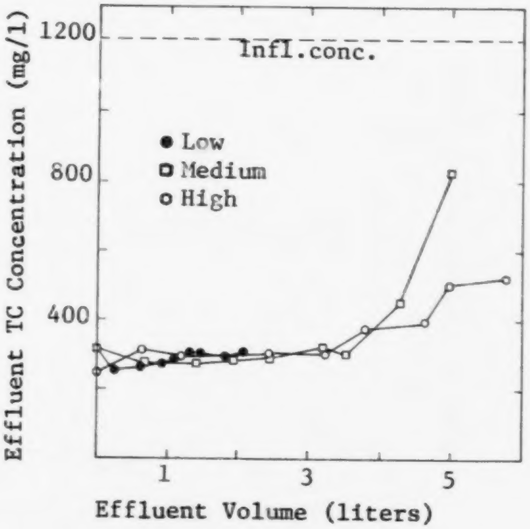

Figure 44A. Breakthrough curve for stream 041A with WVG carbon (solute: TC).

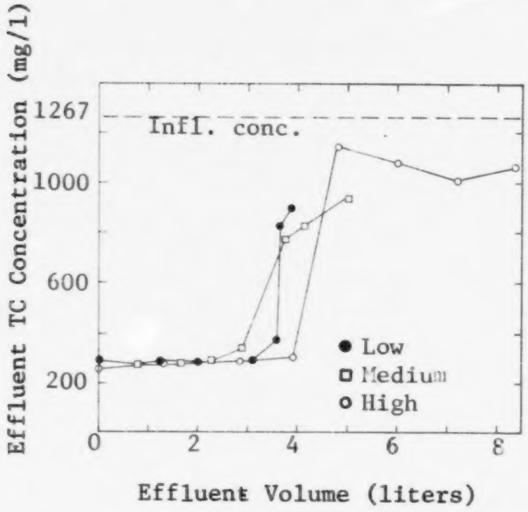

Figure 45A. Breakthrough curve for stream 041A with Filtrasorb-400 carbon (solute: TC).

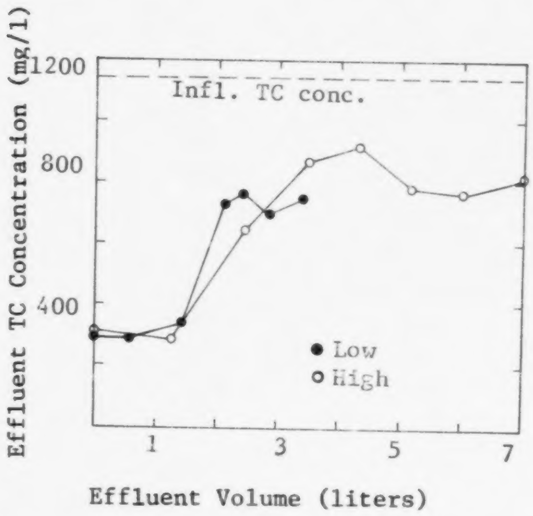

Figure 46A. Breakthrough curve for stream 041A with Monochem carbon, run #104 (solute: TC).

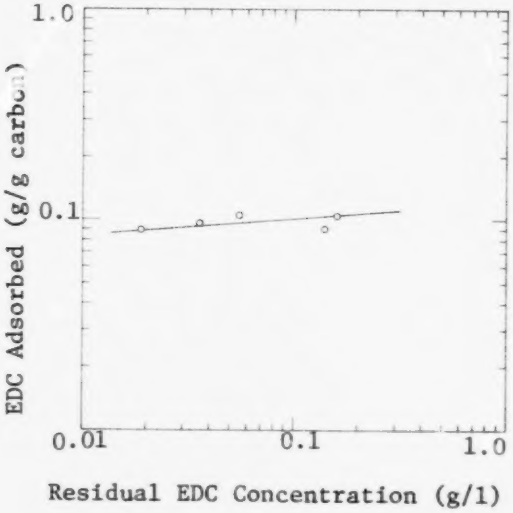

Figure 47A. EDC adsorption isotherm for stream 041A using Monochem soot carbon.

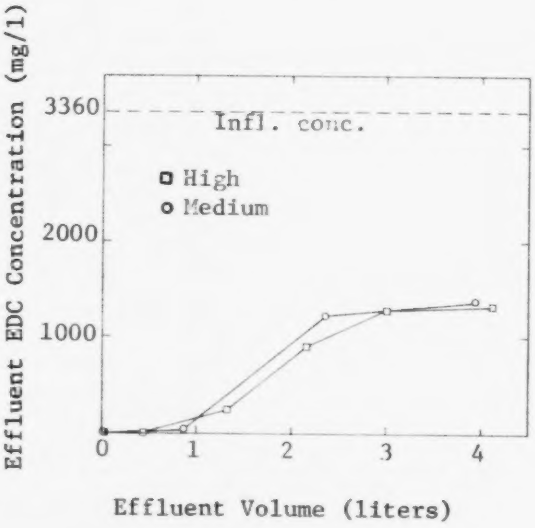

Figure 48A. EDC breakthrough curve for stream 041A using Monochem soot carbon.

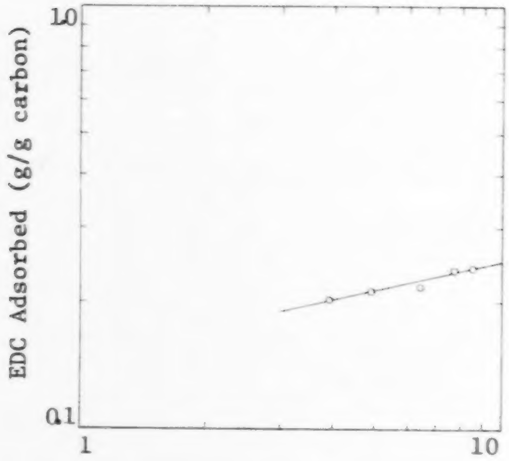

Figure 49A. EDC adsorption isotherm for stream 221A using Monochem soot carbon.

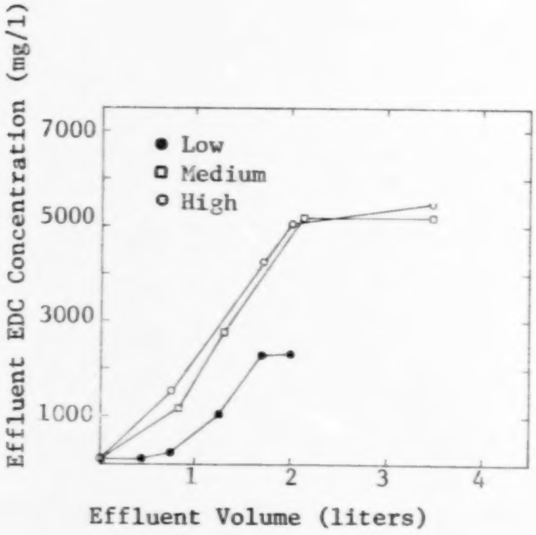

Figure 50A. EDC breakthrough curve for stream 221A using Monochem soot carbon (effluent concentration ≈ 9000 mg/1).

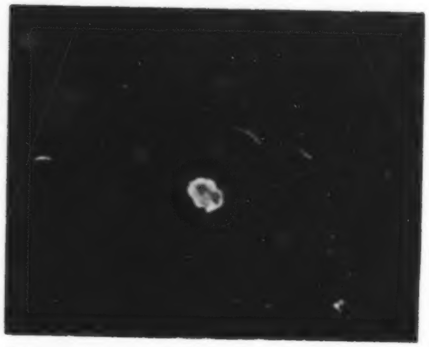

Figure 51A. Sample A (500X)

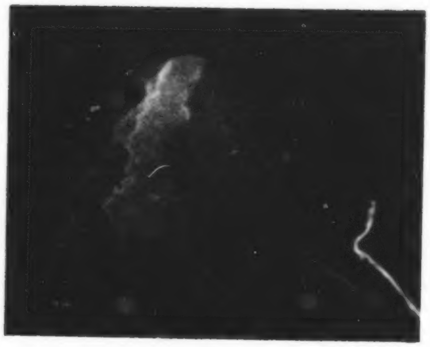

Figure 52A. Sample A (2000X)

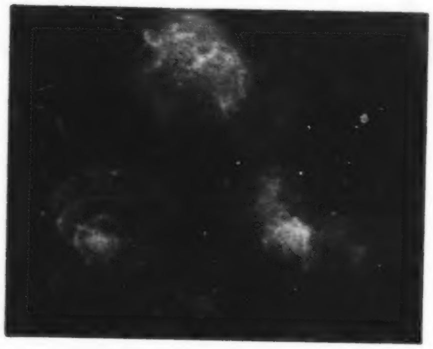

Figure 53A. Sample B (2000X)

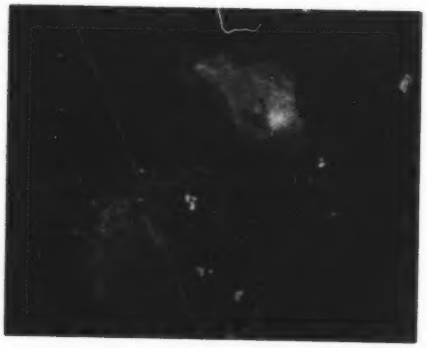

Figure 54A. Sample B (2000X)

Figure 55A. Sample B (5000X)

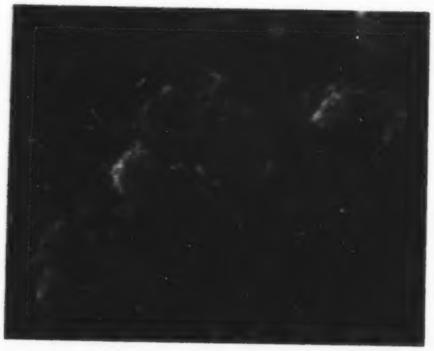

Figure 56A. Sample B (5000X)

Scanning Electron Micrographs

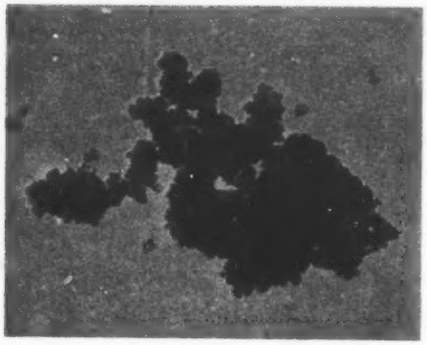

Figure 57A. Sample A (70000X)

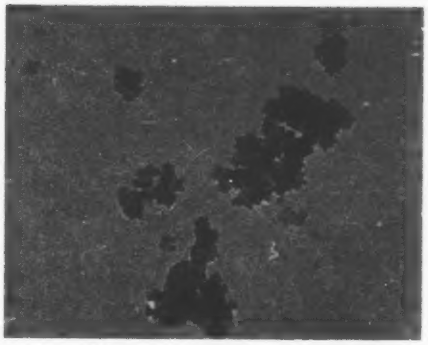

Figure 58A. Sample A (70000X)

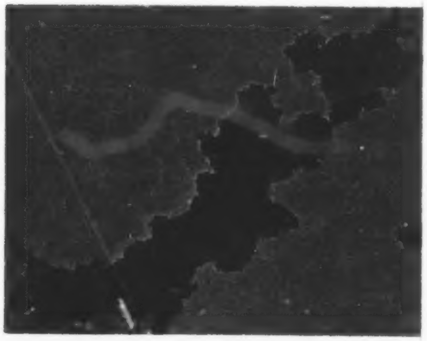

Figure 59A. Sample A (70000X)

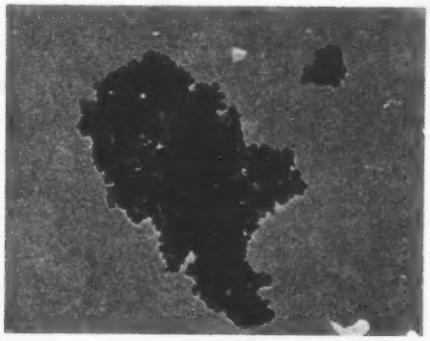

Figure 60A. Sample B (70000X)

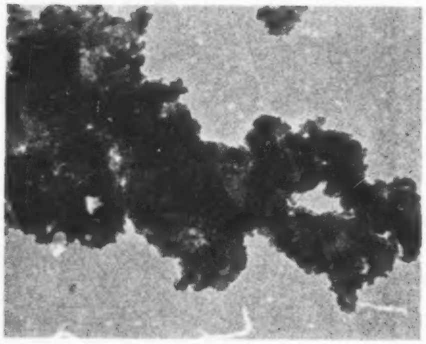

Figure 61A. Sample B (70000X)

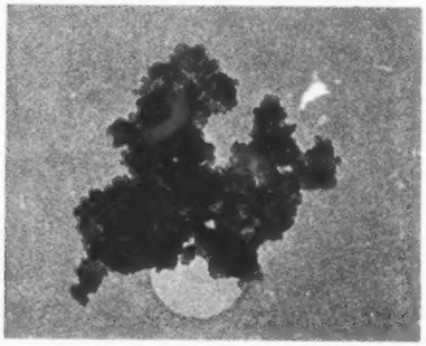

Figure 62A. Sample B (70000X)

Transmission Electron Micrographs

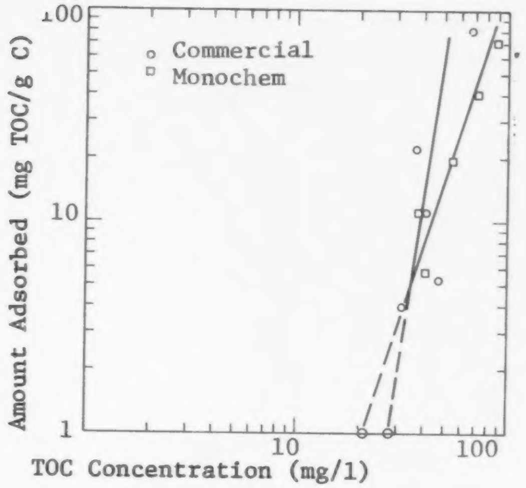

Figure 63A. Adsorption isotherm for EDC.

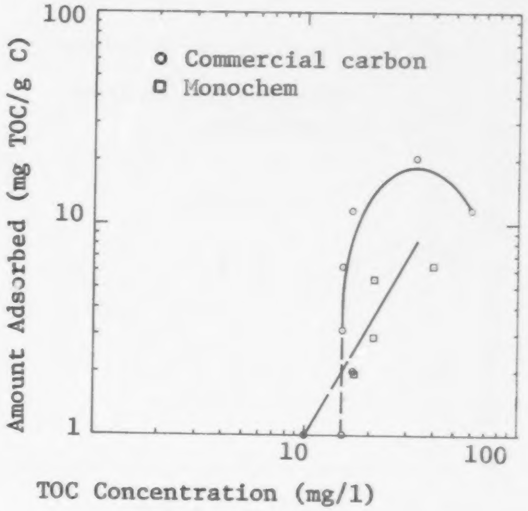

Figure 64A. Adsorption isotherm for benzene.

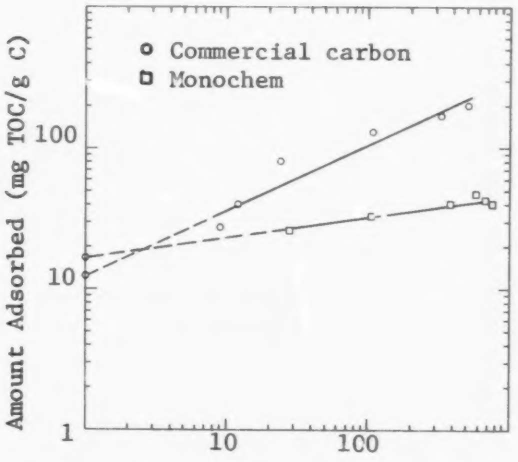

Figure 65A. Adsorption isotherm for phenol, acid solution.

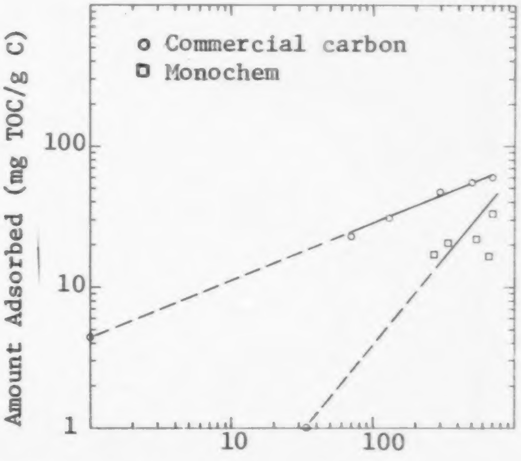

Figure 66A. Adsorption isotherm for phenol, alkaline solution.

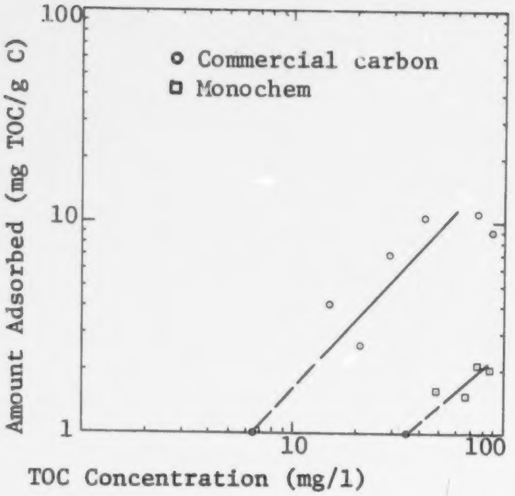

Figure 67A. Adsorption isotherm for chloral hydrate.

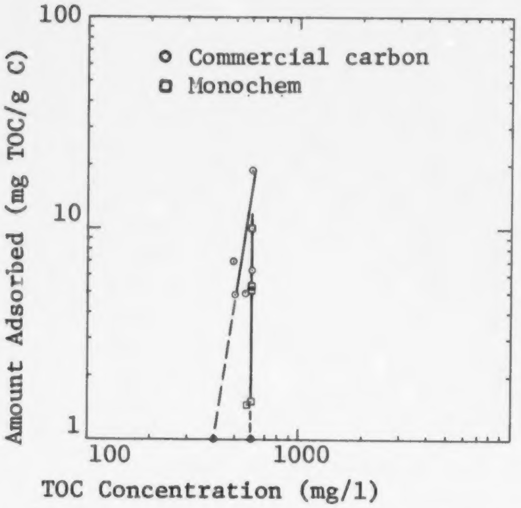

Figure 68A. Adsorption isotherm for toluene di-isocyanate (stream 231A).

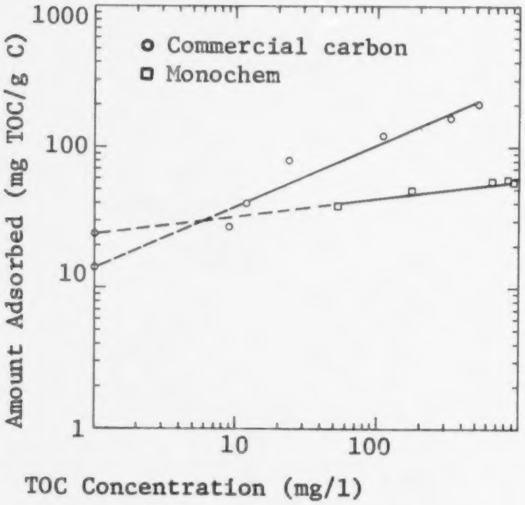

Figure 69A. Adsorption isotherm for phenol on steam activated carbon.

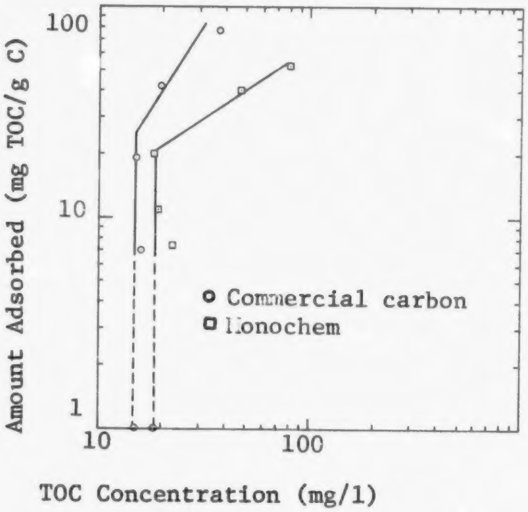

Figure 70A. Adsorption isotherm for benzene on steam activated carbon.

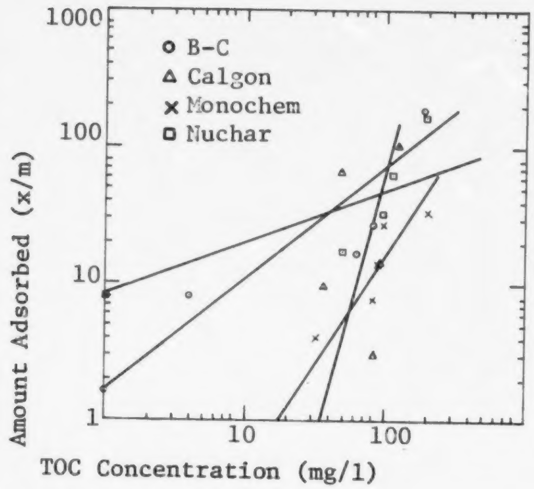

Figure 71A. Adsorption isotherm for stream 231A (treatment: raw).

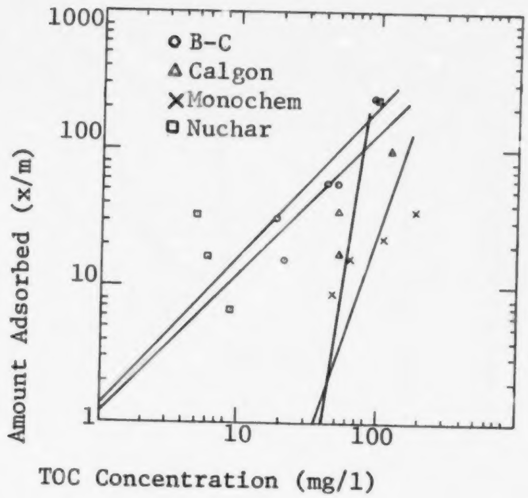

Figure 72A. Adsorption isotherm for stream 231A (treatment: acidified).

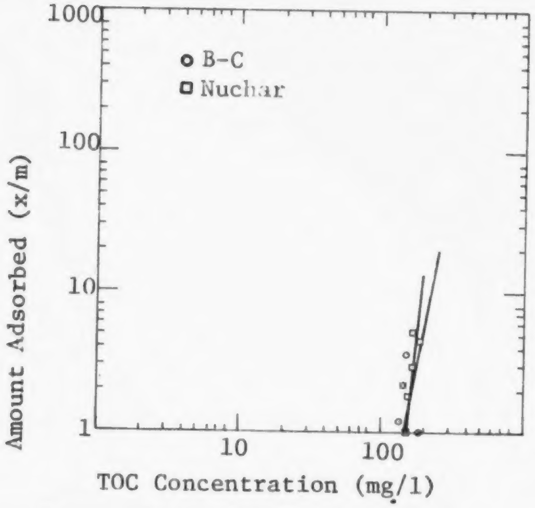

Figure 73A. Adsorption isotherm for stream 231A (treatment: ozonated).

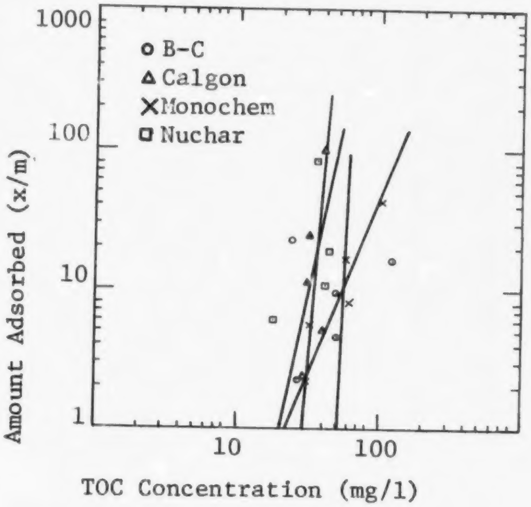

Figure 74A. Adsorption isotherm for stream 231A (treatment: biotreated).

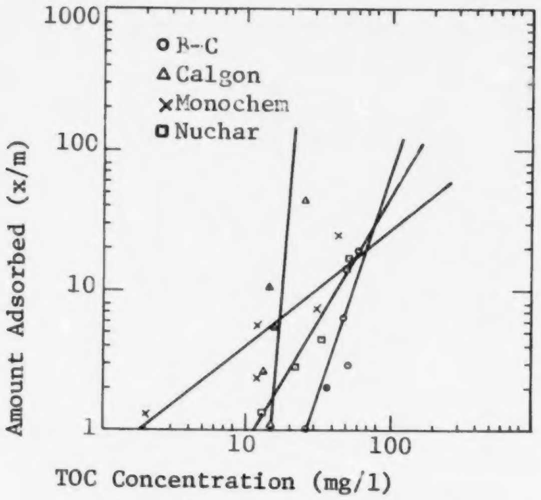

Figure 75A. Adsorption isotherm for stream 231A (treatment: ozonated, biotreated).

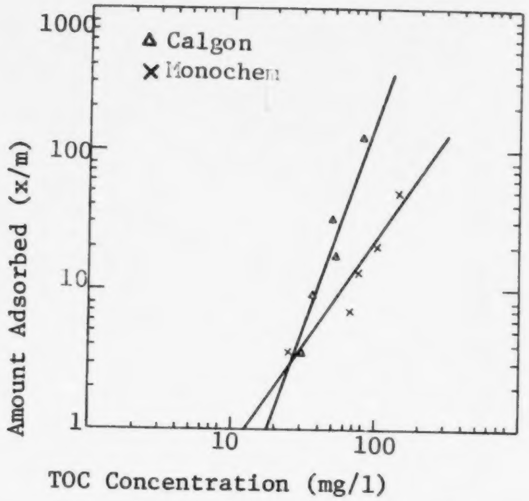

Figure 76A. Adsorption isotherm for stream 231A (treatment: acidified, biotreated).

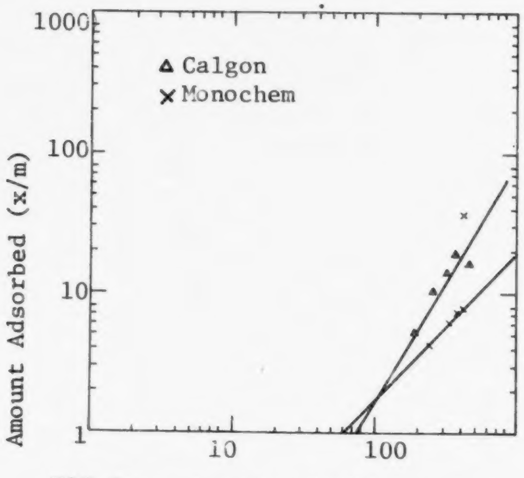

Figure 77A. Adsorption isotherm for stream 221A (treatment: steam stripped bottoms).

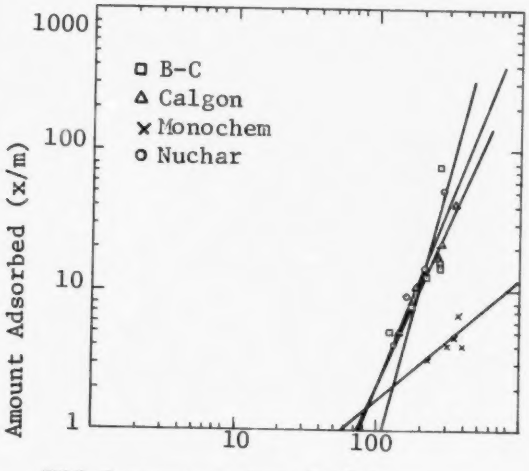

Figure 78A. Adsorption isotherm for stream 221A (treatment: ozonated, steam stripped bottoms).

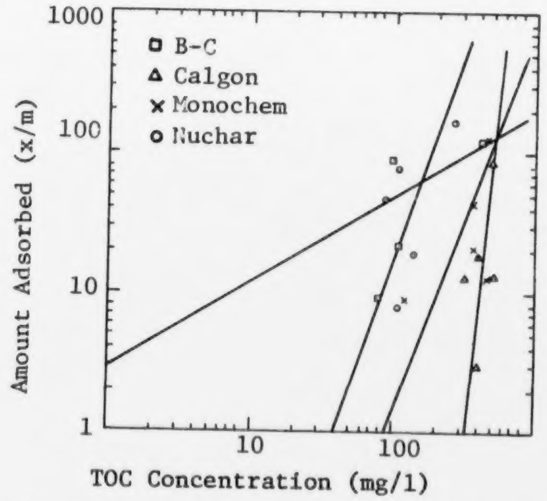

Figure 79A. Adsorption isotherm for stream 231A (treatment: raw).

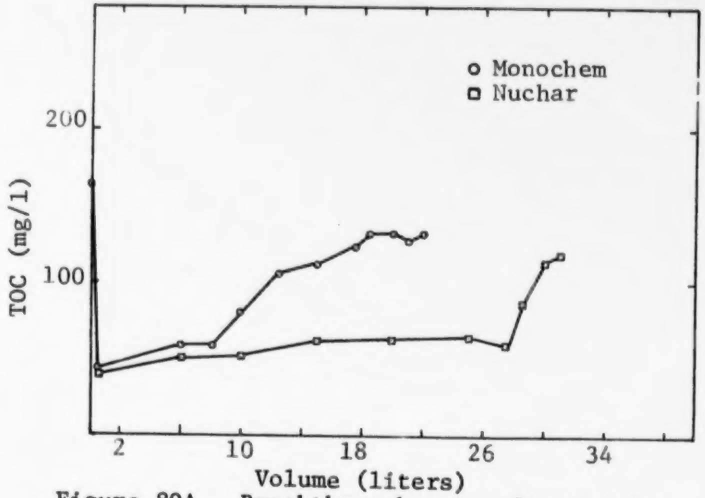

Figure 80A. Breakthrough curve for stream 231A (biotreated), TOC vs. volume.

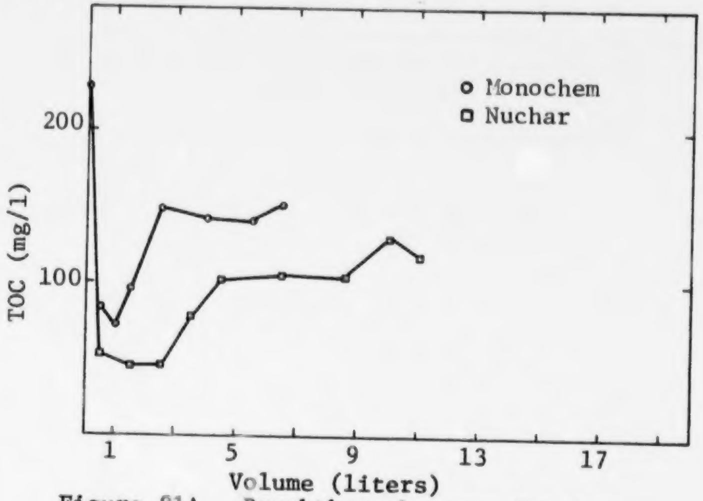

Figure 81A. Breakthrough curve for stream 231A (acidified, biotreated), TOC vs. volume.

BREAKTHROUGH CURVES

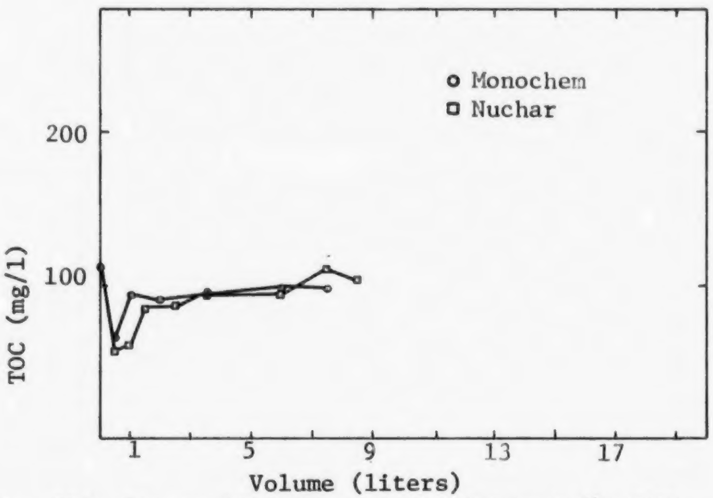

Fig. 82A. Stream 231A (ozonated, biotreated); TOC.

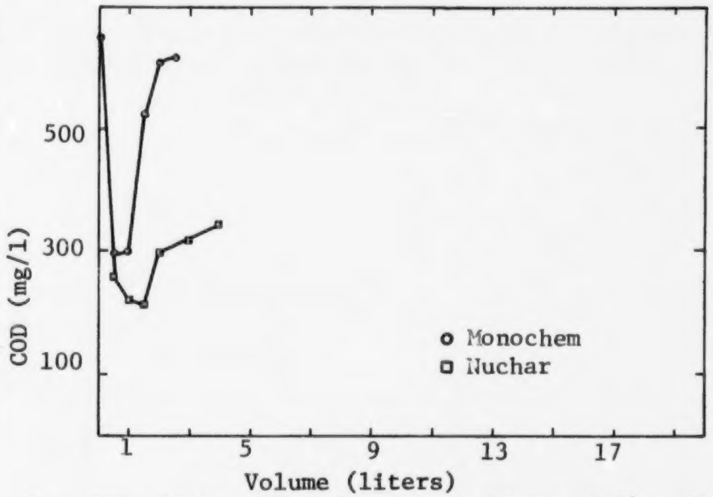

Fig. 83A. Stream 231A (ozonated, biotreated); TOC.

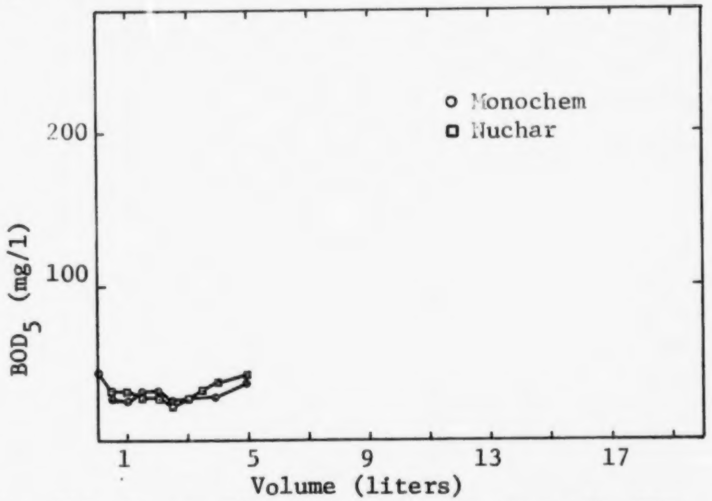

Fig. 84A. Stream 231A (ozonated, biotreated); BOD_5.

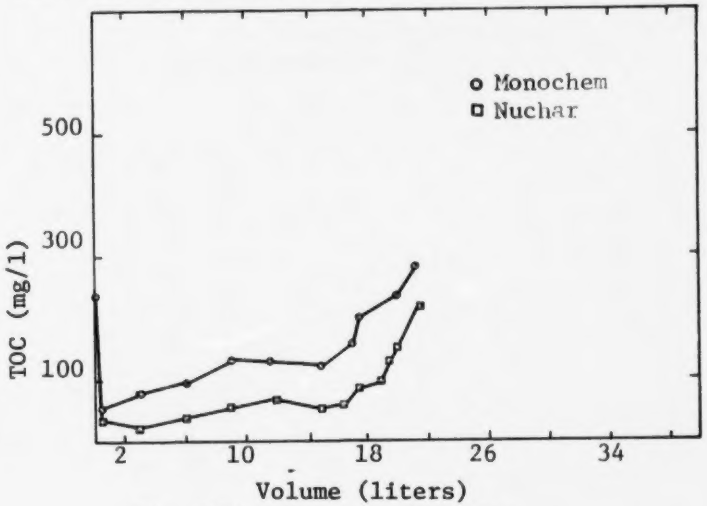

Fig. 85A. Stream 351A; TOC.

BREAKTHROUGH CURVES

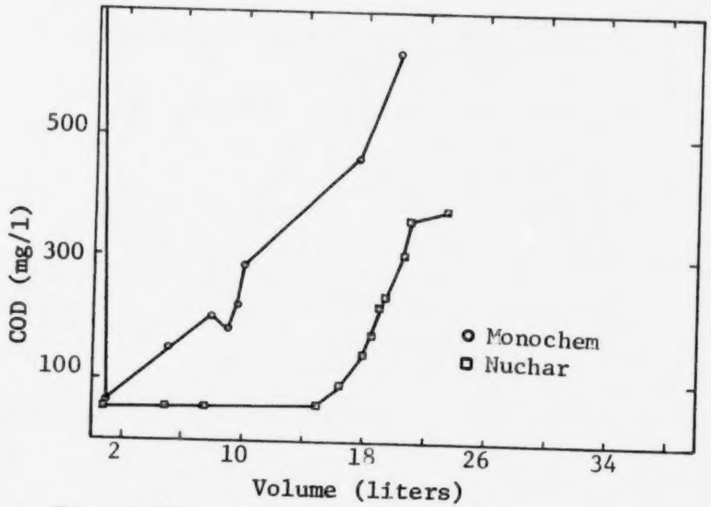

Figure 86A. Stream 351A (raw); COD.

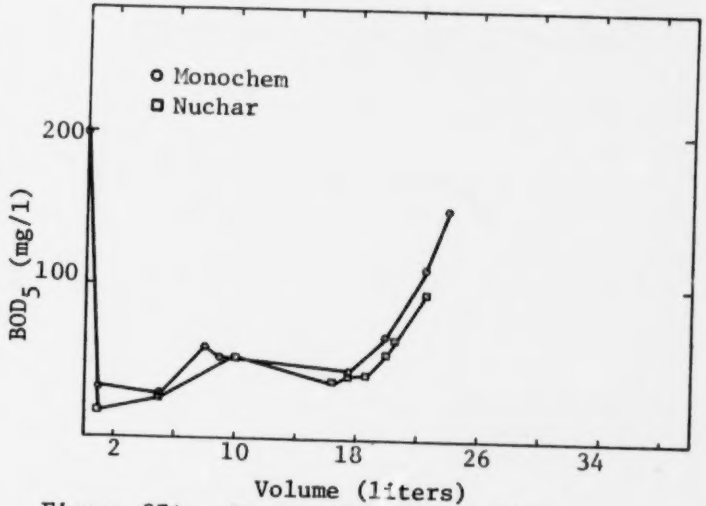

Figure 87A. Stream 351A (raw); BOD_5.

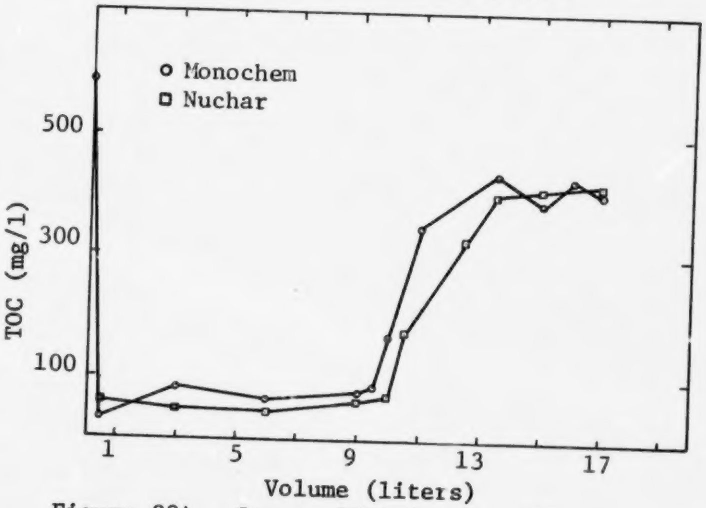

Figure 88A. Stream 231A (raw); TOC.

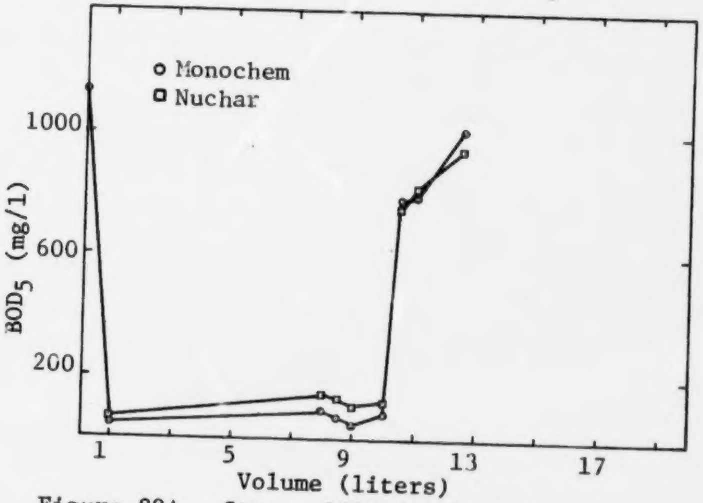

Figure 89A. Stream 231A (raw); BOD_5.

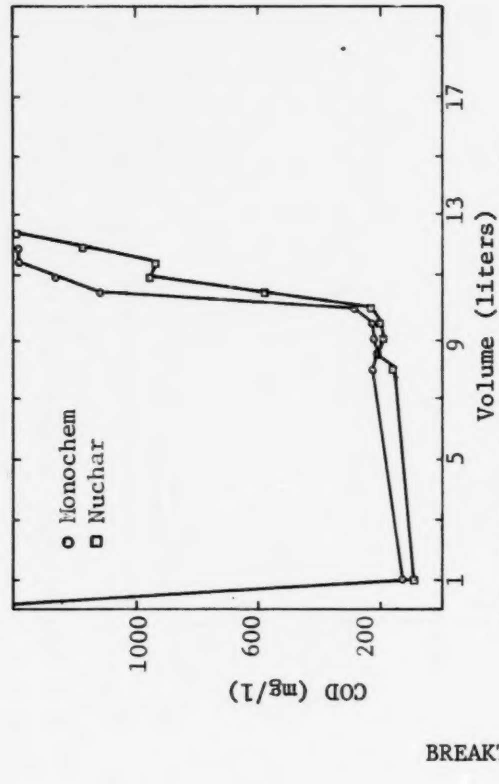

Figure 90A. Stream 231A (raw); COD.

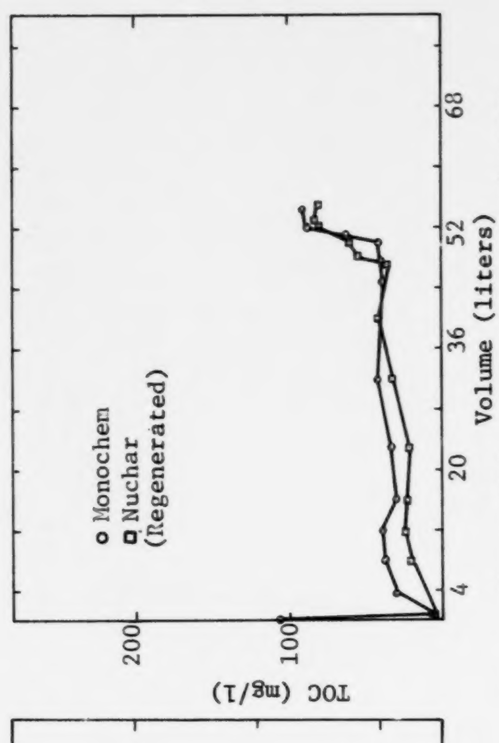

Figure 91A. Stream 231A (raw); TOC.

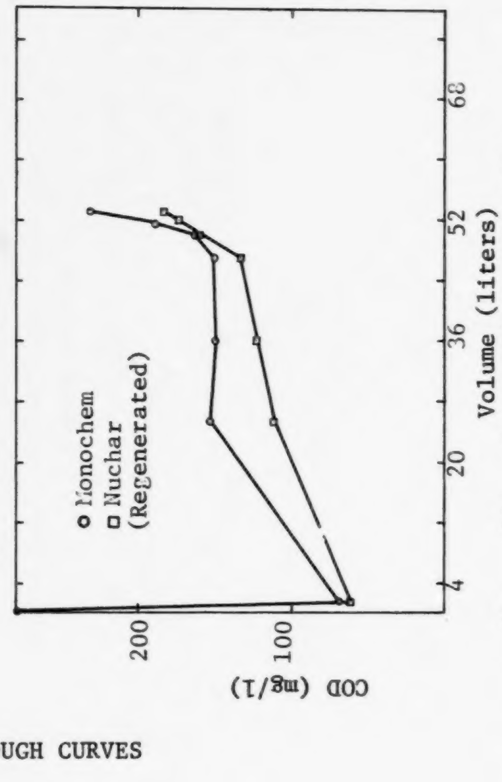

Figure 92A. Stream 231 (raw); COD.

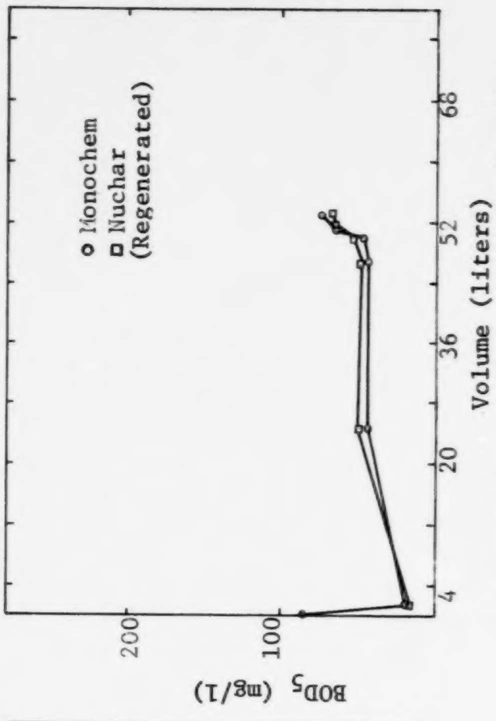

Figure 93A, Stream 231A (raw); BOD_5.

BREAKTHROUGH CURVES

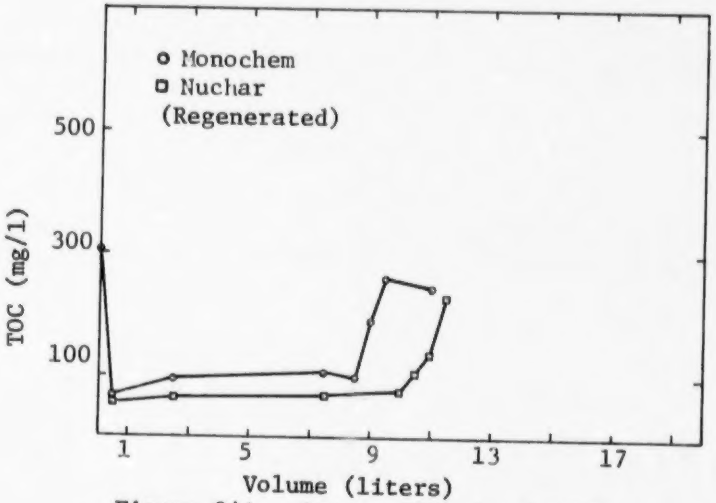

Figure 94A. Stream 351A (raw); TOC.

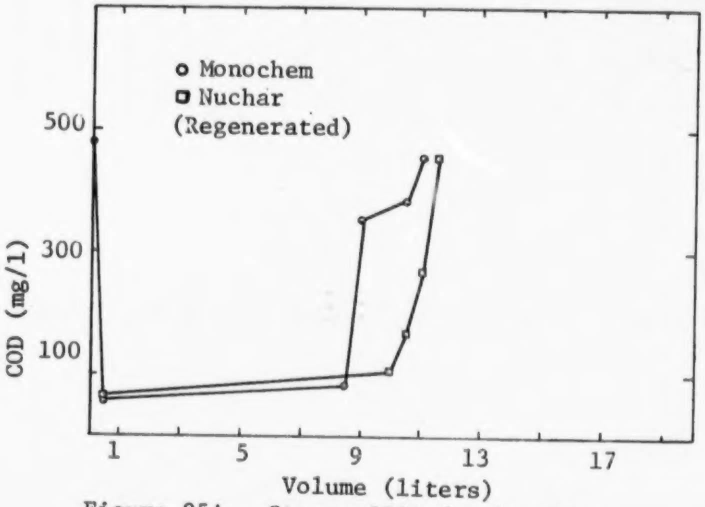

Figure 95A. Stream 351A (raw); COD.

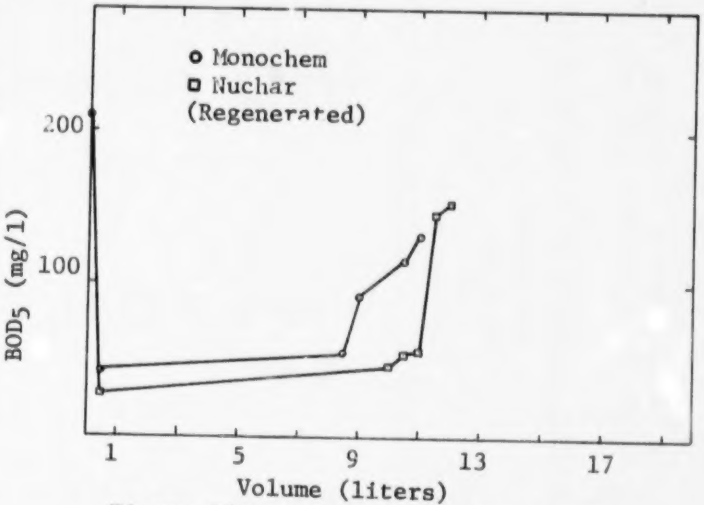

Figure 96A. Stream 351A (raw); BOD_5.

TABLE 1A. ANALYSIS OF COLUMN INFLUENT AND EFFLUENT BY INDIVIDUAL COMPONENT

Type of Carbon: Westvaco Stream: 221A Volume Carbon: 64.8 l
Flow Rate: 1.1 l/min Loading: .74 l/cm^{2}min Carbon Weight: 28.6 l/g
Date: 9/17/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/l) Feed	Concentration (mg/l) Out
6	59	Ethyl Chloride	22.7	0
7	71	Ethyl Chloride	66.0	0
8	83	Ethyl Chloride	37.6	0
9	95	Ethyl Chloride	41.7	18.3
10	101	Ethyl Chloride		283.9
6	69	Vinyl Chloride	0.8	0
7	71	Vinyl Chloride	5.1	0
8	83	Vinyl Chloride	0.5	0
9	95	Vinyl Chloride	2.7	4.3
10	101	Vinyl Chloride		14.5
6	59	Vinylidene Chloride	0	0
7	71	Vinylidene Chloride	0.4	0
8	83	Vinylidene Chloride	0	0
9	95	Vinylidene Chloride	0	0
10	101	Vinylidene Chloride	0	0
7	71	Trans-Dichloroethylene	0	0
8	83	Trans-Dichloroethylene	0	0
9	95	Trans-Dichloroethylene	0	0
10	101	Trans-Dichloroethylene	0	0
6	59	1,1-Dichloro-Ethane	16.8	0
7	71	1,1-Dichloro-Ethane	34.9	0
8	83	1,1-Dichloro-Ethane	23.6	0
9	95	1,1-Dichloro-Ethane	29.9	0
10	101	1,1-Dichloro-Ethane		0
6	59	Chloroform	10.8	0
7	71	Chloroform	16.9	0
8	83	Chloroform	7.6	0
9	95	Chloroform	9.1	0
10	101	Chloroform		0
6	59	Ethylene Dichloride	337.9	0
7	71	Ethylene Dichloride	539.2	0
8	83	Ethylene Dichloride	517.1	0
9	95	Ethylene Dichloride	638.8	0
10	101	Ethylene Dichloride		69.0

(continued)

TABLE 1A (CONTINUED)

Type of Carbon: Westvaco
Flow Rate: 1.1 1/min

Stream: 221A
Loading: .74 1/m^2-min

Volume Carbon: 64.8 1
Carbon Weight: 28.6 1/g
Date: 9.17/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/1) Feed	Out
6	59	1,1,1-Trichloro-Ethane	4.9	0
7	71	1,1,1-Trichloro-Ethane	7.6	0
8	83	1,1,1-Trichloro-Ethane	3.9	0
9	95	1,1,1-Trichloro-Ethane	3.4	0
10	101	1,1,1-Trichloro-Ethane		0
6	59	1,1,2-Trichloro-Ethane	18.0	0
7	71	1,1,2-Trichloro-Ethane	20.5	0
8	83	1,1,2-Trichloro-Ethane	24.0	0
9	95	1,1,2-Trichloro-Ethane	30.5	0
1	2	Chloral Hydrate & Chloral		0
2	11	Chloral Hydrate & Chloral	761.5	0
3	23	Chloral Hydrate & Chloral	696.7	0
4	35	Chloral Hydrate & Chloral	643.0	0
5	47	Chloral Hydrate & Chloral	577.1	0
6	59	Chloral Hydrate & Chloral	218.3 (868.1)	0
7	71	Chloral Hydrate & Chloral	314.6 (995.7)	0
8	83	Chloral Hydrate & Chloral	0 (576.3)	0
9	95	Chloral Hydrate & Chloral	0 (397.5)	0
10	101	Chloral Hydrate & Chloral		322.0

TABLE 2A. ANALYSIS OF COLUMN INFLUENT AND EFFLUENT BY INDIVIDUAL COMPONENT

Type of Carbon: Westvaco
Flow Rate: 1.9 l/min
Stream: 221A
Loading: 1.23 l/m^{2}min
Volume Carbon: 64.8 l
Carbon Weight: 28.6 l/g
Date: 9/27/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/l) Feed	Concentration (mg/l) Out
5	45	Vinyl Chloride	2.3	0
6	56	Vinyl Chloride	8.1	0
7	65	Vinyl Chloride	4.1	0
8	77	Vinyl Chloride	3.1	38.5
4	33	Ethyl Chloride	65.7	0
5	45	Ethyl Chloride	46.9	0
6	56	Ethyl Chloride	75.6	0
7	65	Ethyl Chloride	55.6	83.6
8	77	Ethyl Chloride	55.9	252.7
5	45	Vinylidene Chloride	0	0
6	56	Vinylidene Chloride	0	0
7	65	Vinylidene Chloride	0	0
8	77	Vinylidene Chloride	0	0
5	45	Trans-1,2-Dichloroethylene	0	0
6	56	Trans-1,2-Dichloroethylene	0	0
7	65	Trans-1,2-Dichloroethylene	0	0
8	77	Trans-1,2-Dichloroethylene	0	0
6	56	1,1-Dichloro-Ethane	83.8	0
7	65	1,1-Dichloro-Ethane	139.9	0
8	77	1,1-Dichloro-Ethane	50.1	0
5	45	Chloroform	35.1	0
6	56	Chloroform	171.1	0
7	65	Chloroform	140.0	0
8	77	Chloroform	20.2	0
5	45	Ethylene Dichloride	945.2	0
6	56	Ethylene Dichloride	1146.4	0
7	65	Ethylene Dichloride	1174.8	0
8	77	Ethylene Dichloride	1411.1	611.6
5	45	1,1,1-Trichloro-Ethane	26.4	0
6	56	1,1,1-Trichloro-Ethane	3.5	0
7	65	1,1,1-Trichloro-Ethane	5.0	0
8	77	1,1,1-Trichloro-Ethane	12.1	0

(continued)

TABLE 2A. (CONTINUED)

Type of Carbon: Westvaco
Flow Rate: 1.9 l/min
Stream: 221A
Loading: 1.23 l/m^2min
Volume Carbon: 64.8 l
Carbon Weight: 28.6 l/g
Date: 9/27/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/l) Feed	Concentration (mg/l) Out
5	45	1,1,2-Trichloro-Ethane	12.4	0
6	56	1,1,2-Trichloro-Ethane	17.4	0
7	65	1,1,2-Trichloro-Ethane	19.6	0
8	77	1,1,2-Trichloro-Ethane	9.4	0
3	21	Chloral Hydrate	163.4	0
4	33	Chloral Hydrate	97.6	0
5	45	Chloral Hydrate	321.9	0
6	56	Chloral Hydrate	0	530.7
7	65	Chloral Hydrate	0	229.3
8	77	Chloral Hydrate	0	125.0
3	21	Chloral	345.2	0
4	33	Chloral	458.1	0
5	45	Chloral	1060.2	0
6	56	Chloral	1735.1	0
7	65	Chloral	1311.0	1955.9
8	77	Chloral	1035.1	1574.7
5	45	Propylene Dichloride	54.4	0
6	56	Propylene Dichloride	9.7	0
7	65	Propylene Dichloride	29.4	0
8	77	Propylene Dichloride	20.2	0

TABLE 3A. ANALYSIS OF COLUMN INFLUENT AND EFFLUENT BY INDIVIDUAL COMPONENT

Type of Carbon: Westvaco
Flow Rate: 2.85 l/min
Stream: 221A
Loading: 1.84 l/m^2min
Volume Carbon: 64.8 l
Carbon Weight: 28.6 l/g
Date: 10/1/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/l) Feed	Concentration (mg/l) Out
1	7	Vinyl Chloride	0	0
2	19	Vinyl Chloride	0	0
3	31	Vinyl Chloride	3.6	5.1
4	43	Vinyl Chloride	4.4	10.4
5	55	Vinyl Chloride	5.0	11.1
6	67	Vinyl Chloride	6.3	25.0
1	7	Ethyl Chloride	72.6	0
2	19	Ethyl Chloride	29.4	13.0
3	31	Ethyl Chloride	11.8	202.7
4	43	Ethyl Chloride	33.4	247.6
5	55	Ethyl Chloride	24.7	20.0
6	67	Ethyl Chloride	36.9	108.1
3	31	Vinylidene Chloride	0.5	0
4	43	Vinylidene Chloride	1.4	0
5	55	Vinylidene Chloride	2.3	0
6	67	Vinylidene Chloride	14.6	0
3	31	Trans-1,2-Dichloroethylene	0	0
4	43	Trans-1,2-Dichloroethylene	0	0
5	55	Trans-1,2-Dichloroethylene	0	0
6	67	Trans-1,2-Dichloroethylene	0	0
1	7	1,1-Dichloroethane	237.9	0
2	19	1,1-Dichloroethane	34.6	0
3	31	1,1-Dichloroethane	19.3	0
4	43	1,1-Dichloroethane	33.7	0
5	55	1,1-Dichloroethane	25.3	0
6	67	1,1-Dichloroethane	33.4	52.0
1	7	Chloroform	15.8	0
2	19	Chloroform	23.0	0
3	31	Chloroform	1.6	0
4	43	Chloroform	8.7	0
5	55	Chloroform	3.4	0
6	67	Chloroform	18.0	0

(continued)

TABLE 3A. (CONTINUED)

Type of Carbon: Westvaco
Flow Rate: 2.85 1/min
Stream: 221A
Loading: $1.84\ 1/m^2min$
Volume Carbon: 64.8 1
Carbon Weight: 28.6 1/g
Date: 10/1/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/1)	
			Feed	Out
1	7	Ethylene Dichloride	1338.8	0
2	19	Ethylene Dichloride	1042.9	0
3	31	Ethylene Dichloride	448.7	48.2
4	43	Ethylene Dichloride	1559.4	93.5
5	55	Ethylene Dichloride	1377.0	156.7
6	67	Ethylene Dichloride	1532.5	1699.9
2	19	1,1,2-Trichloro-Ethane	17.4	0
3	31	1,1,2-Trichloro-Ethane	8.7	0
4	43	1,1,2-Trichloro-Ethane	29.1	0
5	55	1,1,2-Trichloro-Ethane	13.1	0
6	67	1,1,2-Trichloro-Ethane	30.0	0
1	7	Chloral Hydrate	83.4	0
2	19	Chloral Hydrate	41.6	0
3	31	Chloral Hydrate	0	0
4	43	Chloral Hydrate	0	111.9
5	55	Chloral Hydrate	0	555.9
6	67	Chloral Hydrate	418.0	699.2
1	7	Chloral	3232.7	0
2	19	Chloral	1231.6	603.1
3	31	Chloral	1170.8	1090.8
4	43	Chloral	862.8	753.5
5	55	Chloral	1401.3	1787.5
6	67	Chloral	1842.2	2284.0
1	7	Propylene Dichloride	1.0	0
2	19	Propylene Dichloride	3.1	0
3	31	Propylene Dichloride	2.9	0
4	43	Propylene Dichloride	0	0
5	55	Propylene Dichloride	34.3	0
6	67	Propylene Dichloride	0	0

TABLE 4A. ANALYSIS OF COLUMN INFLUENT AND EFFLUENT BY INDIVIDUAL COMPONENT

Type of Carbon: Filtrasorb 300 Stream: 221A Volume Carbon: 64.8 l
Flow Rate: 1.1 l/min Loading: .71 l/m^2min Carbon Weight: 28.6 l/g
Date: 9/4/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/l)	
			Feed	Out
4	38	Vinyl Chloride	0.5	0
5	50	Vinyl Chloride	0	0
6	62	Vinyl Chloride	0	0
7	74	Vinyl Chloride	1.0	0.4
8	86	Vinyl Chloride	0.8	5.2
3	26	Ethyl Chloride	22.0	0
4	38	Ethyl Chloride	17.5	0
5	50	Ethyl Chloride	17.5	Trace
6	61	Ethyl Chloride	23.8	0.9
7	74	Ethyl Chloride	20.4	45.5
8	86	Ethyl Chloride	27.2	66.8
5	50	Vinylidene Chloride	0	0
6	62	Vinylidene Chloride	0	0
7	74	Vinylidene Chloride	0.8	0
8	86	Vinylidene Chloride	0	0
5	50	Trans-1,2-Dichloroethylene	0	0
6	62	Trans-1,2-Dichloroethylene	0	0
7	74	Trans-1,2-Dichloroethylene	0	0
8	86	Trans-1,2-Dichloroethylene	0	0
5	50	1,1-Dichloroethane	17.9	0
6	62	1,1-Dichloroethane	24.9	0
7	74	1,1-Dichloroethane	23.2	1.6
8	86	1,1-Dichloroethane	33.5	0
5	50	Chloroform	9.8	0
6	62	Chloroform	1.1	0
7	74	Chloroform	14.0	0
8	86	Chloroform	33.8	0
4	38	Ethylene Dichloride	1,037.6	0
5	50	Ethylene Dichloride	814.0	0
6	62	Ethylene Dichloride	897.3	0
7	74	Ethylene Dichloride	774.3	24.8
8	86	Ethylene Dichloride	1,015.8	47.1

(continued)

TABLE 4A. (CONTINUED)

Type of Carbon: Filtrasorb 300
Flow Rate: 1.1 l/min

Stream: 221A
Loading: .71 l/m^2min

Volume Carbon: 64.8 l
Carbon Weight: 28.6 l/g
Date: 9/4/73

Sample Number	Cumulative Running Time (In Hours)	Component	Concentration (mg/l) Feed	Concentration (mg/l) Out
5	50	1,1,1-Trichloro Ethane	11.2	0
6	62	1,1,1-Trichloro Ethane	0	0
7	74	1,1,1-Trichloro Ethane	2.1	0
8	86	1,1,1-Trichloro Ethane	0	0
4	38	1,1,2-Trichloro Ethane	10.7	0
5	50	1,1,2-Trichloro Ethane	4.8	0
6	62	1,1,2-Trichloro Ethane	1.4	0
7	74	1,1,2-Trichloro Ethane	7.7	0
8	86	1,1,2-Trichloro Ethane	0	0

TABLE 5A. ANALYSIS OF COLUMN INFLUENT AND EFFLUENT BY INDIVIDUAL COMPONENT FOR STREAM 081A

Type of Carbon: Westvaco WVG
Carbon Volume: 28.3 liters
Date: 9/10/74
Loading: 41.6 l/min-m^2
Flow Rate: 3.79 l/m
Carbon Weight: 11.3 kg

Sample Number	Running Time (Hours)	Dichloroethane Concentration (mg/l) Influent	Dichloroethane Concentration (mg/l) Effluent	1,1,2,2-Tetrachloroethane Concentration (mg/l) Influent	1,1,2,2-Tetrachloroethane Concentration (mg/l) Effluent	Methylene Chloride Concentration (mg/l) Influent	Methylene Chloride Concentration (mg/l) Effluent	Trans-Dichloroethylene Concentration (mg/l) Influent	Trans-Dichloroethylene Concentration (mg/l) Effluent
1	3	80.47	0.12	315.39	64.50	0.15	0.02	139.10	0.02
2	6	45.62	2.60	326.29	6.32	0.13	0.05	3.74	0.10
3	9	152.46	0.09	191.61	7.00	0.18	0.04	7.80	-
4	12	76.00	25.10	10.75	24.00	0.34	0.06	0.94	0.50
5	15	250.00	42.00	106.50	25.00	1.32	0.17	2.42	0.75
6	18	111.48	0.48	138.00	0.68	0.32	0.07	6.96	1.14
7	21	166.00	156.00	18.00	36.00	0.20	0.11	12.40	2.62
8	24	172.00	264.88	18.00	2.70	0.36	0.07	4.40	8.23
9	27	4.96	144.00	50.00	10.20	0.07	0.06	0.32	0.62
10	30	0.40	162.00	29.50	8.50	0.54	0.01	0.06	8.60
11	33	188.00	142.00	9.50	20.50	0.32	0.84	7.80	11.80
12	36	162.00	94.00	10.20	3.18	0.13	0.09	11.40	17.20
13	39	42.34	128.00	60.38	3.95	0.24	0.10	1.77	18.54
14	42	42.46	34.39	36.00	3.04	0.13	-	0.75	29.91
15	45	23.55	62.91	3.80	-	0.07	0.22	0.02	0.03
16	48	6.16	85.04	-	-	0.62	0.34	0.03	0.03
17	51	5.43	36.71	42.63	3.96	0.40	0.23	0.22	5.42
18	54	56.67	33.05	49.80	2.62	0.12	-	17.80	7.22
19	57	6.48	50.00	50.40	3.84	0.12	0.42	0.11	6.80
20	60	2.12	0.06	20.48	1.56	0.32	56.33	0.17	1.22

(continued)

TABLE 5A (CONTINUED)

Type of Carbon: Westvaco WVG
Carbon Volume: 28.3 liters
Date: 9/10/74
Loading: 41.6 l/min-m^2
Flow Rate: 3.79 l/m
Carbon Weight: 11.3 kg

Sample Number	Running Time (Hours)	Dichloroethane Concentration (mg/l) Influent	Dichloroethane Concentration (mg/l) Effluent	1,1,2,2-Tetrachloroethane Concentration (mg/l) Influent	1,1,2,2-Tetrachloroethane Concentration (mg/l) Effluent	Methylene Chloride Concentration (mg/l) Influent	Methylene Chloride Concentration (mg/l) Effluent	Trans-Dichloroethylene Concentration (mg/l) Influent	Trans-Dichloroethylene Concentration (mg/l) Effluent
1	3	2.45	0.72	-	2.09	26.54	0.65	8.75	0.25
2	6	0.73	0.02	4.58	0.02	12.60	0.19	6.47	0.23
3	9	1.10	0.18	2.28	2.76	19.38	0.15	14.75	0.09
4	12	0.88	0.23	-	-	3.22	0.33	3.46	0.14
5	15	0.56	0.55	0.14	-	1.34	0.18	2.80	0.20
6	18	0.60	0.56	0.04	-	1.37	0.06	2.52	0.02
7	21	1.60	1.81	0.35	-	3.23	0.23	3.88	0.17
8	24	1.84	2.30	-	-	2.22	0.24	3.92	0.09
9	27	0.23	4.20	33.20	-	1.31	0.39	1.98	0.14
10	30	1.96	8.40	-	0.05	0.23	0.31	1.42	0.21
11	33	3.28	4.20	-	-	2.14	0.38	3.46	0.24
12	36	2.00	4.20	0.21	-	2.10	0.38	2.96	0.22
13	39	2.10	2.35	2.05	-	11.45	0.39	7.48	0.41
14	42	2.65	4.47	2.35	-	20.37	0.28	11.93	0.24
15	45	0.05	0.05	2.79	10.78	21.84	22.82	0.23	0.24
16	48	0.45	0.11	2.00	7.87	22.04	25.20	15.05	0.24
17	51	0.86	3.18	0.15	0.13	0.26	0.24	1.34	0.18
18	54	1.12	3.12	0.92	0.02	3.93	0.24	1.36	0.09
19	57	0.52	6.80	2.21	0.02	1.48	0.30	3.21	0.39
20	60	0.25	11.55	0.23	-	2.10	0.28	2.64	0.14

TABLE 6A. EFFECT OF KEROSENE DIESEL OIL SOLVENT ON REMOVAL OF MAJOR ORGANICS FROM STREAM 161A - Removal of EDC

	Total EDC		Amount		
Date	In (mg/1)	Out (mg/1)	Removed (mg/1)	Percent Removed	Ratio H_2O:Solvent
10/23/74	920	356	564	61	13.3:1
10/11/74	193	20	173	90	13.7:1
10/11/74	127	19	108	85	9.1:1
10/31/74	208	47	161	77	9.1:1
11/21/74	126	43	83	66	9.1:1
11/25/74	300	35	265	88	5.5:1
12/11/74	297	81	216	73	5.5:1
12/16/74	931	70	861	92	5.5:1
12/04/74	56	92	(36)	(64)	5.5:1
1/06/75	316	16	300	95	5.5:1
12/02/74	324	36	288	89	3.7:1 & 5.5:1
12/10/74	1804	40	1764	98	3.7:1
12/17/74	407	13	394	97	3.7:1
1/07/75	23	<1	--	99	3.7:1

TABLE 7A. EFFECT OF KEROSENE DIESEL OIL SOLVENT ON REMOVAL OF MAJOR ORGANICS FROM STREAM 161A - Removal of 1,1,2-Trichloroethane

	Total 1,1,2 TCE		Amount		
Date	In (mg/1)	Out (mg/1)	Removed (mg/1)	Percent Removed	Ratio H_2O:Solvent
10/23/74	105	16	89	85	18.3:1
10/11/74	355	30	325	92	13.7:1
10/11/74	269	36	233	87	9.1:1
10/31/74	127	21	106	83	9.1:1
11/21/74	57	8	49	86	9.1:1
11/25/74	88	3	85	97	5.5:1
12/11/74	157	6	151	96	5.5:1
12/16/74	155	2	153	99	5.5:1
12/04/74	90	14	76	84	5.5:1
1/06/75	73	2	71	97	5.5:1
12/02/74	180	<1	--	99	3.7:1 & 5.5:1
12/10/74	135	20	115	85	3.7:1
12/17/74	30	3	27	90	3.7:1
1/07/75	177	3	174	98	3.7:1

TABLE 8A. EFFECT OF KEROSENE DIESEL OIL SOLVENT ON REMOVAL OF MAJOR ORGANICS FROM STREAM 161A - Removal of 1,1,2,2-Tetrachloroethane

Date	Total Sym. Tetra. In (mg/l)	Total Sym. Tetra. Out (mg/l)	Amount Removed (mg/l)	Percent Removed	Ratio H_2O:Solvent
10/23/74	22	6	16	93	18.3:1
10/11/74	197	2	195	99	13.7:1
10/11/74	147.9	19.3	128.6	87	9.1:1
10/31/74	--	--	--	--	9.1:1
11/21/74	22	2	20	91	9.1:1
11/25/74	56	0	56	100	5.5:1
12/11/74	32	1	31	97	5.5:1
12/16/74	5	0	5	100	5.5:1
12/04/74	39.3	0	39.3	100	5.5:1
	59	2	57	96.6	5.5:1
1/06/75	115	3	112	97.4	5.5:1
12/02/74	49.4*	0.4*	49*	99	3.7:1 & 5.5:1
12/10/74	162.1	0	162.1	100	3.7:1
12/17/74	17	0	17	100	3.7:1
1/07/75	95	3	92	96.8	3.7:1